THE JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

OCTOBER 1, 1942

MONTHLY PUBLICATION DEVOTED TO THE ARTS AND SCIENCES RELATED TO THE SILICATE INDUSTRIES

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Publication Office: 20th & Northampton Sts., Easton, Pa.
Editorial Office: 2525 N. High St., Columbus, Ohio
Committee on Publications: D. E. Sharp, *Chairman;* E. E. Marbaker, J. B. Austin, G. H. Spencer-Strong, Ross C. Purdy.
Entered as second-class matter at the post office at Easton, Pa., under the act of March 3, 1879. Published monthly.
Subscription fifteen dollars ($15.00) a year. Single numbers $1.50
(Foreign and Canadian postage, 50¢ additional on subscriptions)
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ELECTRIC FURNACE BOROALUMINATE*

By H. N. Baumann, Jr., and C. H. Moore, Jr.

Abstract

Boroaluminate has been produced as a crystalline material by electric furnace fusion. The crystal form is orthorhombic; $N_g = 1.625$, $N_m = 1.603$, and $N_p = 1.589$; composition, $2B_2O_3 \cdot 9Al_2O_3$; unit cell, $a = 15.0$ a.u., $b = 7.5$ a.u., and $c = 5.67$ a.u. Other crystallographic and X-ray data are given in detail. It appears to melt incongruently, and it is analogous in several ways to mullite.

The physical properties of fusion-cast refractory boroaluminate compositions are enumerated.

I. Introduction

This paper presents studies conducted on a crystalline compound of boric oxide and aluminum oxide formed by fusion in an electric furnace. The method for the manufacture of this compound was first described in a patent[1] issued in 1938. Mellor,[2] as late as 1924, stated that the "evidence for the existence of definite aluminum borates is very unsatisfactory." Ebelmen,[3] in the course of his classical syntheses of artificial crystals in 1851, concluded that alumina mixed with boric oxide is not altered when it is heated in a pottery kiln but that with borax the alumina was changed to corundum. The eminent petrographer, Mallard,[4] thirty-six years later examined a number of Ebelmen's fusions and discovered among them small acicular crystals whose optical properties he described and to which he assigned the formula, $3Al_2O_3 \cdot B_2O_3$ or $(AlO)_3BO_3$.

With the present knowledge of the high viscosity of B_2O_3 at its melting point and with the great range in temperature between the melting points of B_2O_3 and Al_2O_3 as demonstrated by Cole,[5] Mellor's reason for the unsatisfactory evidence of a synthetic boroaluminate is apparent. Approaching the problem at the opposite end of the system B_2O_3–Al_2O_3, Benner[1] made the production of boroaluminate practical by dissolving the boric oxide in molten alumina in an electric furnace. In the center of a pig produced in that manner, a number of well-developed acicular crystals, up to 2 cm. long, were found. Figure 1 is a photomicrograph of broken sections of these crystals, which were excellent specimens for examination; most of the physical and optical data reported herewith were obtained by the microscope and X-ray diffraction examination of these crystals. Their molecular formula appears to be $2B_2O_3 \cdot 9Al_2O_3$ rather than $3Al_2O_3 \cdot B_2O_3$ as originally reported. This formula is verified not only by chemical analysis, but as will be shown later, it is also consistent with other data.

II. Crystallographic and Optical Properties of Boroaluminate

Boroaluminate crystallizes in the orthorhombic system. The dominant form is the orthorhombic prism (110) which, coupled with an elongation parallel to the c-axis, gives the crystals an acicular-to-prismatic habit. The occasional development, however, of large macropinicoidal (100) faces in conjunction with the prism yields well-shaped tabular crystal.s No distinct terminations could be observed.

The crystals exhibit a perfect cleavage parallel to (001) anda poor cleavage parallel to (111). They have an uneven-to-subconchoidal fracture and vitreous luster. The hardness, measured by the Knoop microindentor on the macropincoid has a value of 785 parallel to the direction of elongation and of 704 normal to the direction of elongation. This makes boroaluminate almost identical in hardness to quartz, the latter mineral showing a Knoop indentation number of

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Refractories Division). Received June 29, 1942.

[1] R. C. Benner and H. N. Baumann, Jr., "Refractory Material," U. S. Pat. 2,118,143, May 24, 1938; *Ceram. Abs.*, **17** [8] 882 (1938).

[2] J. W. Mellor, Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. V, p. 102. Longmans, Green & Co., London, 1924, x + 1004 pp.; *Ceram. Abs.*, **4** [2] 47 (1925).

[3] J. J. Ebelmen, *Compt. Rend.*, **32**, 331 (1851); *Ann. Chim. Phys.*, [3] 33–62 (1851).

[4] E. Mallard, *Compt. Rend.*, **105**, 1260 (1887).

[5] S. S. Cole and N. W. Taylor, "System Na_2O–B_2O_3, I," *Jour. Amer. Ceram. Soc.*, **18** [2] 55–58 (1935).

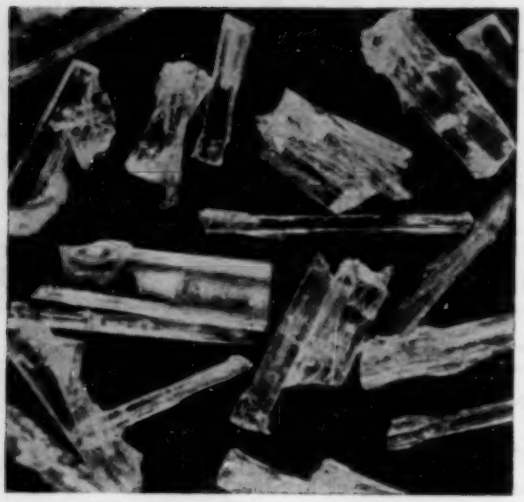

FIG. 1.—Boroaluminate crystal, ×11.

TABLE I

PETROGRAPHIC DATA ON MELTS OF VARYING COMPOSITIONS AND OF VARIOUS TYPES OF FUSIONS

No. 1: B_2O_3 3%, Al_2O_3 97%; cast fusion

α-Al_2O_3 crystals and glass; no boroaluminate crystals present.

No. 2: B_2O_3 5%, Al_2O_3 95%; bubbles (almost instantaneous cooling)

Consists entirely of α-Al_2O_3 crystals and glass.

No. 3: B_2O_3 10%, Al_2O_3 90% (see Fig. 2*A*); cast fusion

Poorly crystallized skeletal types of α-Al_2O_3; crystals being replaced along lines of weak crystallization, parallel to base and vertical axis by sheaves of fibrous boroaluminate; boroaluminate fibers, nearly 0.5 mm. long, comprise approximately 25% of crystalline constituents.

No. 4: B_2O_3 20%, Al_2O_3 80% (see Fig. 2*B*); fusion (rapidly cooled)

Generally same as fusion containing 10% of B_2O_3 in No. 3: boroaluminate crystals larger (up to 1 mm. long) and more completely replacing α-alumina, but greater amount of B_2O_3 still in boroalumina glass; rapid cooling has produced skeletal crystals and inhibited complete crystallization of boroaluminate.

No. 5: B_2O_3 20%, Al_2O_3 80% (see Fig. 2*C*); cast fusion

Section consists entirely of radiating fibrous acicular-to-columnar crystals of tightly interlocking boroaluminate; crystals vary in length from 0.75 mm. in fibrous types to more than 2 mm. for columnar crystals; crystals show chiefly a plane parallel orientation parallel to plane of casting although a few isolated columnar crystals are normal to this plane; crystal size and habit vary from fibrous structure to more massive columnar crystals toward center of casting.

No. 6: B_2O_3 35%, Al_2O_3 65% (see Fig. 2*D*); cast fusion

Randomly oriented columnar crystals of boroaluminate in brown high-index glass.

No. 7: Boroaluminate crystal; cone fusion

Thin sections of boroaluminate crystal heated to above its melting point and quickly cooled; a few acicular crystals of boroaluminate, irregular crystals of α-Al_2O_3, and high-index glass; there is at least a partial dissociation of boroaluminate to alumina and glass at high temperatures.

710 parallel to the *c*-axis and 790 normal to the *c*-axis. The specific gravity of boroaluminate is 2.93

Indistinct penetration twins are noted occasionally, in which the trace of the composition plane is apparently parallel to (100). Many of the cavity-filling crystals are intergrown in various positions. This growth is not to be confused with twinning inasmuch as the crystal intergrowths, as far as can be determined, follow no definite law.

Thin sections, which were cut parallel to the direction of elongation, normal to the direction of elongation, and oblique to elongation, yielded the following optical data: Optic plane (010); positive (+) elongation; $Z = C$, $y = b$, and $x = a$. The mineral is optically positive (+) $2V = 87°$. The positive acute bisectrix, Z, is normal to (001).

Powders of the pure crystals show $N_g = 1.625$, $N_m = 1.603$, and $N_p = 1.589$; $N_g - N_p = 0.036$. These data check closely with those values first determined for boroaluminate by Mallard[4] fifty years ago.

Crystals, forming *in situ* from the melt, occur as fibrous, radiating-to-matlike, tightly intermeshed masses, colorless in polarized light, but they show a strong birefringence under crossed Nicols. These fibrous-to-prismatic crystals of boroaluminate have a marked resemblance to sillimanite and mullite in their optical orientation and crystallographic properties.

Table I shows the results of the petrographic examination of melts of varying compositions and of various types of fusions; these data are also shown in Fig. 2.

III. X-Ray Diffraction Examination

Boroaluminate crystals were examined by the powder diffraction method as well as by the rotation method. Table II shows the results of the powder diffraction examination; as would be expected from an orthorhombic crystal, the pattern contains a large number of lines. The photogram from which these data were measured and calculated was made by means of a Seemann Debye-Scherrer camera, using copper K-α radiation.

The X-ray rotation photographs were made by

TABLE II

POWDER DIFFRACTION DATA FOR BOROALUMINATE INTERPLANAR SPACINGS AND ESTIMATES OF RELATIVE INTENSITIES

Estimated intensity*	Interplanar spacing (a.u.)	Estimated intensity*	Interplanar spacing (a.u.)
M	5.99	*MS*	1.835
S	5.19	*M*	1.77
W†	4.76	*W*	1.712
MS	4.34	*M*	1.685
W†	3.76	*W*	1.595
S	3.64	*W*	1.558
W	2.86	*S*	1.518
S	2.71	*W*	1.481
M	2.51	*W*	1.455
W	2.31	*M*	1.414
W	2.25	*S*	1.336
MS	2.17	*MS*	1.307
MS	2.11	*M*	1.251
W	2.01	*W*	1.232
W	1.94	*W*	1.188

* *VW*, very weak; *W*, weak; *M*, medium; *MS*, medium strong; *S*, strong.
† Diffuse.

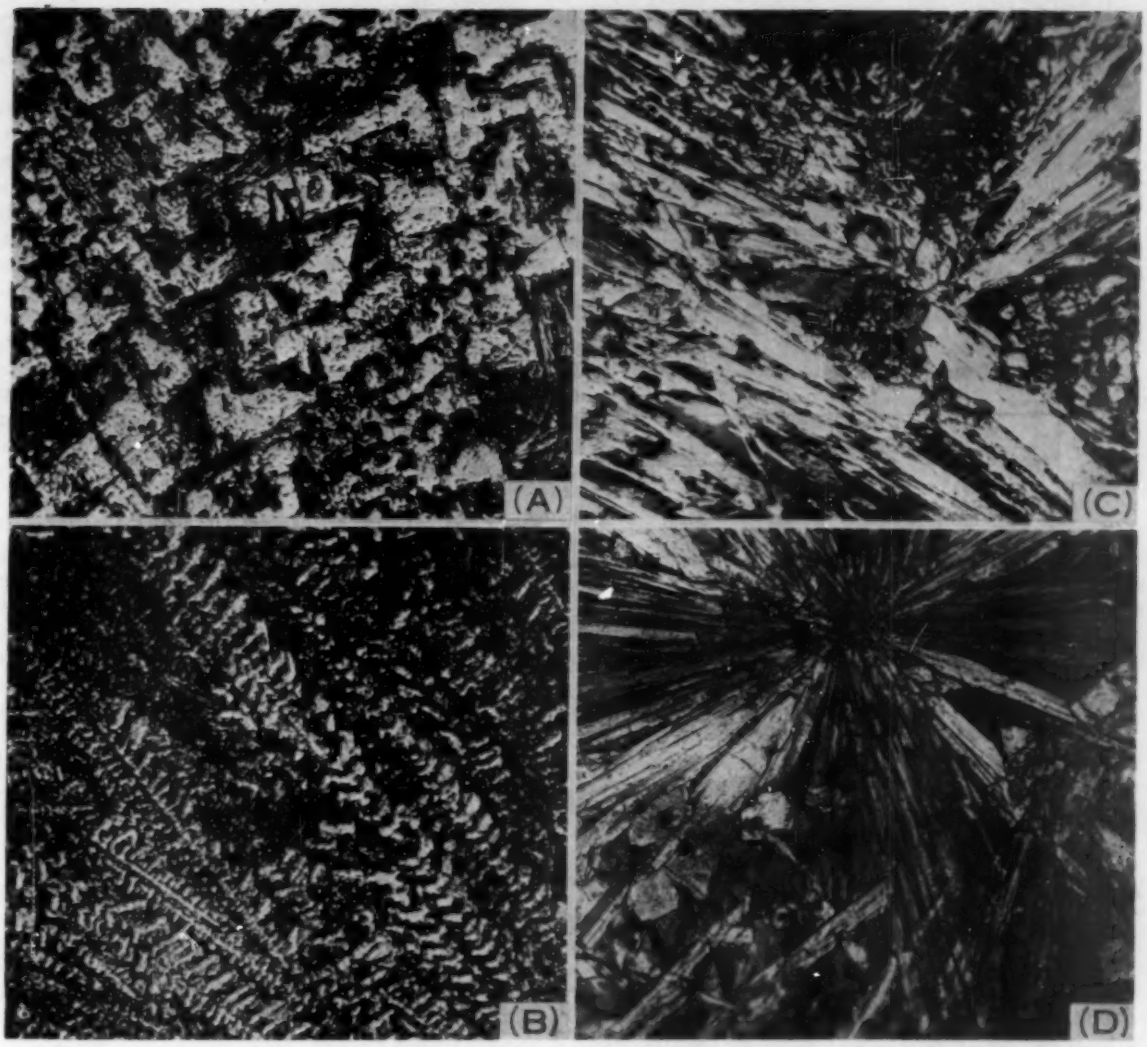

FIG. 2.—Thin-section photomicrographs; each crossed Nicols, selenite plate: (*A*) Cast fusion B_2O_3 10%, Al_2O_3 90%, ×150; (*B*) rapidly cooled small fusion, B_2O_3 20%, Al_2O_3 80%, ×80; (*C*) cast fusion B_2O_3 20%, Al_2O_3 80%, ×80; (*D*) cast fusion B_2O_3 35%, Al_2O_3 65%, ×80.

revolving crystals, respectively, on their three orthorhombic axes, using copper K-α radiation. The layer photogram gave calculated dimensions for the unit cell as follows: a = 15.0 a.u., b = 7.5 a.u., c = 5.67 a.u. Using the molecular weight of $2B_2O_3 \cdot 9Al_2O_3$ and the specific gravity of 2.93, the number of molecules in the unit cell is calculated to be 1.1, a value so close to unity that the unit cell probably contains only one molecule and the formula, $2B_2O_3 \cdot 9Al_2O_3$, is probably correct.*

IV. System Al_2O_3–B_2O_3

The resemblance between boric oxide and silica as glassforming oxides and the analogy between various comparable binary systems containing B_2O_3 and SiO_2, respectively, as components are worth noting. The writers found that boroaluminate and mullite appear to resemble each other crystallographically, and like mullite, boroaluminate appears to melt incongruently, although the temperature of incongruent melting was not definitely determined. Figure 3 shows the results of several experiments. The pouring-point curve, which was obtained by optical readings of the temperature of the stream of three different boric oxide-alumina fusions as they were poured, probably gives a rough idea of what the liquidus may be in that composition range. With a B_2O_3 content greater than 35%, the melt not only becomes too viscous to pour but the electrical resistant of the bath increases rapidly with higher amounts of B_2O_3. The cone fusion curve for the

* The formula $3Al_2O_3 \cdot B_2O_3$ originally assigned to boroaluminate appears to be incorrect. In using the original chemical analyses and specific gravity determinations, the writers had some indication that the formula might be $B_2O_3 \cdot 4Al_2O_3$, but the chemical analysis of more thoroughly cleaned crystals indicates that $2B_2O_3 \cdot 9Al_2O_3$ is the correct formula. It is, of course, quite possible for alumina compounds formed by high-temperature fusion to have unusual compositions, for example, beta-alumina with the proposed formula, $Na_2O \cdot 11Al_2O_3$.

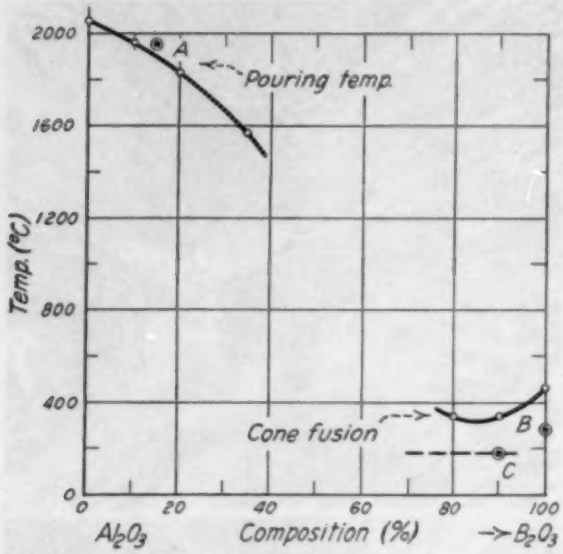

FIG. 3.—Pouring-point and cone-fusion curves: *A*, observed melting point for boroaluminate crystal; *B*, boric oxide melting point (after Cole[5]); *C*, temperature at which blistering occurred.

higher percentages of B_2O_3 indicates a possible eutectic. The high viscosity of boric oxide makes the cone fusion method rather unsatisfactory, but as a preliminary survey of the system Al_2O_3–B_2O_3, Fig. 3 gives a partial idea of what the liquidus curve may approximately be.

The curves of Fig. 3 of course are not those of a constitution diagram, but they may have a relation to the actual constitution diagram, similar to the relation of the classical cone fusion diagram obtained by Seger to the alumina-silica diagram finally developed by Bowen and Greig. It is interesting to note point *A*, Fig. 3, which was the observed melting point for a boroaluminate crystal. An examination of this fused sample after it had been cooled rapidly indicated that the melting had been incongruent, the products being α-alumina, a high boric oxide glass, and some secondary boroaluminate (see Table I, No. 7). This incongruent melting is further complicated because the liquid from the incongruent melting is high in boric oxide, and boric oxide has an appreciable vapor pressure at the temperature of incongruent melting. Point *B* is the melting point of boric oxide as given by Cole,[5] but the cone deformation occurred considerably higher on account of the high viscosity of boric oxide. The line drawn through point *C* parallel to the abscissas indicates the temperature at which the cones high in boric oxide blistered; as the cone containing only B_2O_3 did not blister, this line probably marks the temperature of the eutectic between B_2O_3 and boroaluminate. Point *C* blistered to the greatest degree so that it probably marks the approximate eutectic composition.

The only boroaluminate found in nature is the rare mineral jeremejevite, which has the chemical formula of $BAlO_3$. This mineral is not only different from artificial boroaluminate chemically but its crystalline properties are in no way comparable. It occurred to the authors that, because nothing like jeremejevite was produced by the fusion of boric oxide and alumina, this mineral must bear a relation to artificial boroaluminate, similar to that of sillimanite, andalusite, and kyanite to mullite and that if jeremejevite were heated it would be converted to artificial boroaluminate ($2B_2O_3 \cdot 9Al_2O_3$) and a glass. The only jeremevite samples in existence, however, are a few small museum specimens so that it was not possible to verify this hypothesis.*

V. Physical Properties and Uses of Boroaluminate

Boroaluminate fusions which are cast into refractory blocks are characterized by a dense structure free from pipes and holes. Castings with the original composition of boric oxide 20% and alumina 80% have a linear coefficient of expansion of 4.2×10^{-6} per °C. between room temperature and 1400°C., a value almost identical with that of fusion cast mullite. Under a load of 25 lb. per sq. in., such brick showed no deformation at 1500°C. In a car-tunnel type of spalling test in which 9-in., standard-size cast brick were heated to 1200°C. and subjected to heat shock by quick periodic withdrawal of the car into the open, cast boroaluminate type of brick, which varied in composition from 10 to 35% of boric oxide, withstood failure three to four times as long as cast mullite brick.

In addition to use as a refractory article, boroaluminate appears to have possible uses as a ceramic raw material. It is insoluble in water and quite stable chemically.

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* Private communication. (1) The American Museum of Natural History, New York, N. Y., does not have a single specimen (F. H. Pough, Curator of Geology and Mineralogy); (2) the Smithsonian Institution, United States National Museum, Washington, D. C., has only a single small specimen (E. P. Henderson, Assistant Curator of Geology); and (3) Harvard University has a single specimen about 3 cm. long by 1 cm. in diameter which was obtained within the last year "at an exceedingly high price" (Harry Berman, Curator, the Mineralogical Museum, Harvard University). This appears to be the complete inventory of jeremejevite specimens in the United States.

STRUCTURE OF SODIUM BORATE GLASSES AS AFFECTED BY TEMPERATURE*

By A. E. Badger, H. C. Johnson, and J. O. Kraehenbuehl

Abstract

A series of sodium borate glasses, varying from 0 to 30% of Na_2O in chemical composition and containing 0.1% of cobalt oxide as coloring agent, was prepared by melting in platinum and casting disks of proper size for measurement of spectral transmission up to the softening temperature of the glass. A General Electric automatic recording photoelectric spectrophotometer was used for the measurements. The change in color of the chromophore was correlated with the structures of the glasses, which have been deduced by Biscoe and Warren. Measurements made at higher temperatures indicated that abrupt changes in spectral transmission occurred near the transformation temperatures of the various glasses. Transmission curves of glasses at room temperature showed variations at about 15% of Na_2O, which were correlated with the known breaks in physical properties of these glasses occurring near this composition. Theoretical deductions indicated that stable configurations in the glasses should exist near those compositions containing 10 and 20% of Na_2O.

I. Introduction

The structure of glass as depicted by Zachariasen[1] has been confirmed by extensive investigations of Warren[2] and his colleagues, who have correlated a number of physical properties of glass with the results of their X-ray determinations of glass structure.

Another method that has been used to study the constitution of glass is by visual observation and quantitative measurements of the various colors produced in different glasses when a small amount of coloring oxide is incorporated in the glass composition.[3] The coloring oxide thus acts as an indicator of the internal structure of the glass.

The present writers have studied the change in the structure of glass which is produced when it is heated. The series of sodium borate glasses used was chosen for study because their structure is known.[4] Cobalt oxide was selected as the coloring agent or "indicator" of the structural changes occurring in the glass. These color changes were measured with a General Electric automatic recording photoelectric spectrophotometer.

II. Preparation of Glasses

Table I shows the chemical compositions of a series of sodium borate glasses which were calculated from the glass batches.

The glasses were made by mixing the proper amounts of c.p. Na_2CO_3 and H_3BO_3 with the addition of Co_3O_4 equal to 0.1% of the weight of glass formed, melting the batches in platinum crucibles, casting disks of the glass in a mold, and annealing the glass. The samples were then ground and polished, using absolute alcohol as a carrier for the abrasive and polishing material. The samples were approximately 5 mm. thick and 25 mm. square when completed.

Table I

Chemical Compositions of Glasses

Glass designation	Na_2O (%)	B_2O_3 (%)
A	0	100
B	5	95
C	10	90
D	12.5	87.5
E	15	85
F	17.5	82.5
G	20	80
H	30	70

III. Method for Spectral Transmission Tests at Higher Temperatures

The spectral transmissions of the glasses at room temperature were obtained by placing the specimens in the regular holder of the recording spectrophotometer. For tests at higher temperatures, a small furnace was designed to fit in the apparatus as shown in Fig. 1. The glass sample, *S*, was placed between two sections of nickel tubing, *N*, which were wound with a Chromel heating element, *W*. Asbestos tape, *A*, was used to insulate the Chromel wire. A thermocouple, *T*, was placed in contact with the surface of the glass to measure its temperature. Windows of fused quartz glass, *G*, were used to close the ends of the tubular opening through the furnace, which was mounted in insulating blocks, *B* and *C* (the upper block was removable to permit the insertion of the samples). A steel case, *D*, held the assembly in proper position.

There was a considerable loss in intensity of light on passing through the furnace. This loss of intensity, which was due mainly to reflection and absorption by the fused quartz windows, made a correction necessary

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio April 21, 1942 (Glass Division). Received April 13, 1942.

[1] W. H. Zachariasen, "Atomic Arrangement in Glass," *Jour. Amer. Chem. Soc.*, **54** [10] 3941–51 (1932); *Ceram. Abs.*, **12** [4] 145; [12] 416 (1932).

[2] B. E. Warren, "Summary of Work on Atomic Arrangement in Glass," *Jour. Amer. Ceram. Soc.*, **24** [8] 256–61 (1941).

[3] For example, see W. Weyl, "Chemistry of Colored Glass," *Glass Ind.*, **18** [3] 73–78; [4] 117–20; [5] 167–71 (1937); *Ceram. Abs.*, **16** [6] 170; [7] 201; [8] 239 (1937).

[4] J. Biscoe and B. E. Warren, "X-Ray Diffraction Study of Soda-Boric Oxide Glass," *Jour. Amer. Ceram. Soc.*, **21** [8] 287–93 (1938).

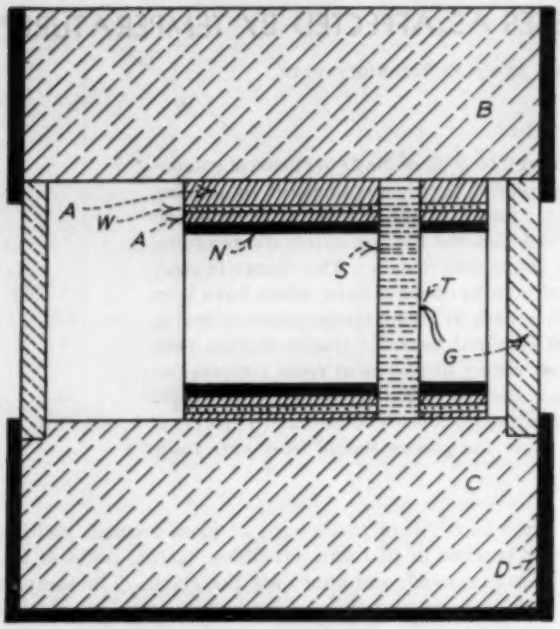


FIG. 1.—Furnace for measurements of spectral transmission of glass at temperatures up to glass softening point; *S*, glass sample; *N*, nickel tubing; *W*, electric heating element; *A*, asbestos tape; *T*, thermocouple; *G*, fused quartz windows; *B*, *C*, insulating blocks; *D*, steel casing.

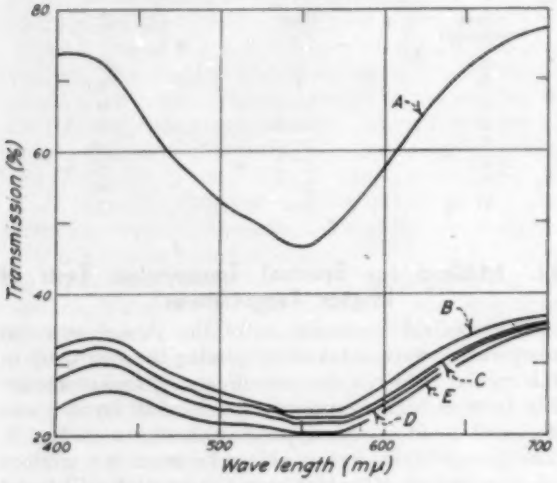


FIG. 2.—Spectral transmission curves of glass D; curve *A*, true transmission in regular holder; *B*, *C*, *D*, *E*, apparent transmission in furnace at 25°, 250°, 300°, and 350°C., respectively.

so that the actual transmission of the glass sample could be obtained from measurements made on the sample in the furnace. These corrections were obtained for each glass sample first by obtaining the true transmission with the sample in position in the regular holder of the spectrophotometer and then by measuring the transmission with the sample in the furnace. Factors for various wave lengths were computed

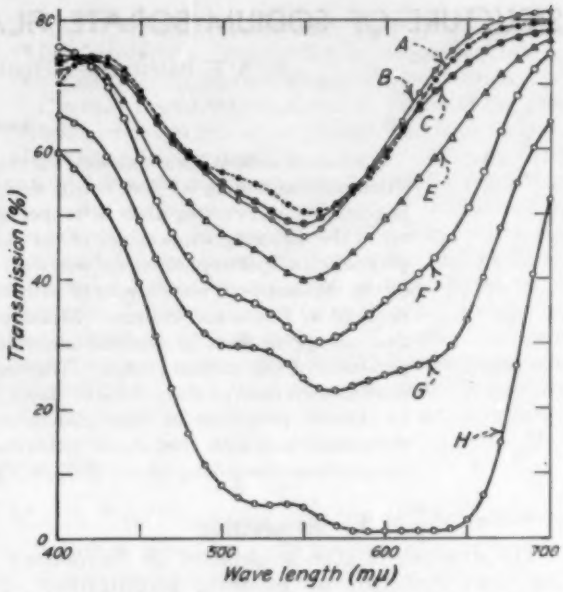


FIG. 3.—Spectral transmission curves of sodium borate glasses at room temperature.

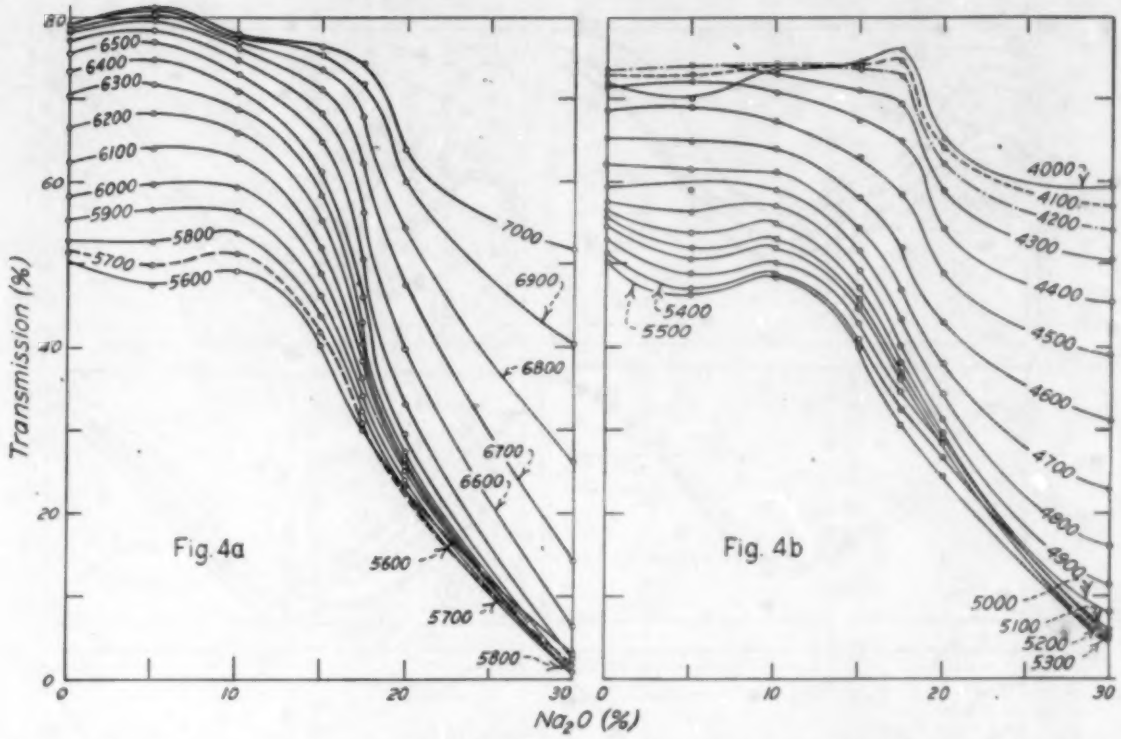
Curve	Na_2O (%)	B_2O_3 (%)	Curve	Na_2O (%)	B_2O_3 (%)
A	0	100	*E*	15	85
B	5	95	*F*	17.5	82.5
C	10	90	*G*	20	80
			H	30	70

from these curves, by means of which the true spectral transmission of the glass in the furnace could be determined from the transmission curve that was obtained with the glass in position in the furnace.

Figure 2 gives an example of these data; the true transmission of glass sample *D* is shown by curve *A*, whereas curve *B* refers to the transmission measured with the sample in the furnace at room temperature. Curves *C*, *D*, and *E* give the transmissions, with the sample in the furnace, at 250°, 300°, and 350°C., respectively. Factors were obtained at a series of wave lengths which would convert curve *B* (of Fig. 2) to the true transmission shown by curve *A*. These factors were assumed to be reliable for converting the transmission curves at higher temperatures (as *C*, *D*, and *E*) to the true transmissions at these temperatures. The assumption that these factors remain constant at higher furnace temperatures is not strictly correct, inasmuch as changes in the refractive index of the glasses in the furnace system and the consequent change in reflection from their surfaces are neglected.

IV. Spectral Transmission Tests at Room Temperature

Figure 3 shows spectral transmissions at room temperature of the series of sodium borate glasses with cobalt oxide indicator, the compositions extending from 100% of B_2O_3 (curve *A*) to 70% of B_2O_3 plus 30% of Na_2O (curve *H*). The curves, *A* through *H* (Fig. 3) correspond to the designations of the glasses given in Table I. The decrease in transmission for



FIGS. 4*a* AND 4*b*.—Percentage transmission of light of constant wave length shown as function of soda content of glass; sharp decrease in transmission evident at all wave lengths when Na_2O exceeds 10 to 15% (wave length in Angstrom units).

most wave lengths, as Na_2O is increased, is evident from this series of curves, the glasses changing color from purple to blue. The most pronounced change is found in the wave-length region of 500 to 680 mμ. The change in color produced by the presence of soda is not merely proportional to the Na_2O content, but it also undergoes a rapid change when the soda exceeds 10 to 15%. This sudden change is more clearly shown by the series of curves in Figs. 4*A* and 4*B*, which were obtained from Fig. 3 by plotting the percentage of transmission at certain constant wave lengths against the soda content. The decrease in transmission when the amount of Na_2O exceeds 15% is evident. The obvious inference is that a change in glass structure occurs in this range of chemical composition.

V. Spectral Transmission Tests at Higher Temperature

Using the furnace equipment described previously, the spectral transmissions of the sodium borate glasses could be obtained up to the softening point of the glass samples. The results of such tests, with corrections applied as described in section III, are shown in the curves of Figs. 5*A* through 5*H*.

The following observations are noteworthy: (*a*) Except for the pure B_2O_3 glass, a decrease in transmission is produced by a rise in temperature. Pure B_2O_3 glass first decreases in transmission and then increases as the temperature is raised (Fig. 5*A*); (*b*) the glass containing 10% of Na_2O showed little effect of temperature on transmission (Fig. 5*C*); and, (*c*) the most pronounced color change occurred in the glass containing 20% of Na_2O, which changed from purple to blue with increase in temperature (Fig. 5*G*).

The data shown in Figs. 5*A* through 5*H* are replotted in Figs. 6*A* through 6*H* as percentage of transmission at various wave lengths against temperature. These curves show more clearly the effects of temperature on the transmission at the various wave lengths. The curves in Fig. 6 exhibit quite sharp breaks in many cases at temperatures which cannot be determined closely because of the small number of points present. It is possible, however, to estimate these temperatures as shown in Table II.

The significance of these temperatures will be considered in the following discussion. The various

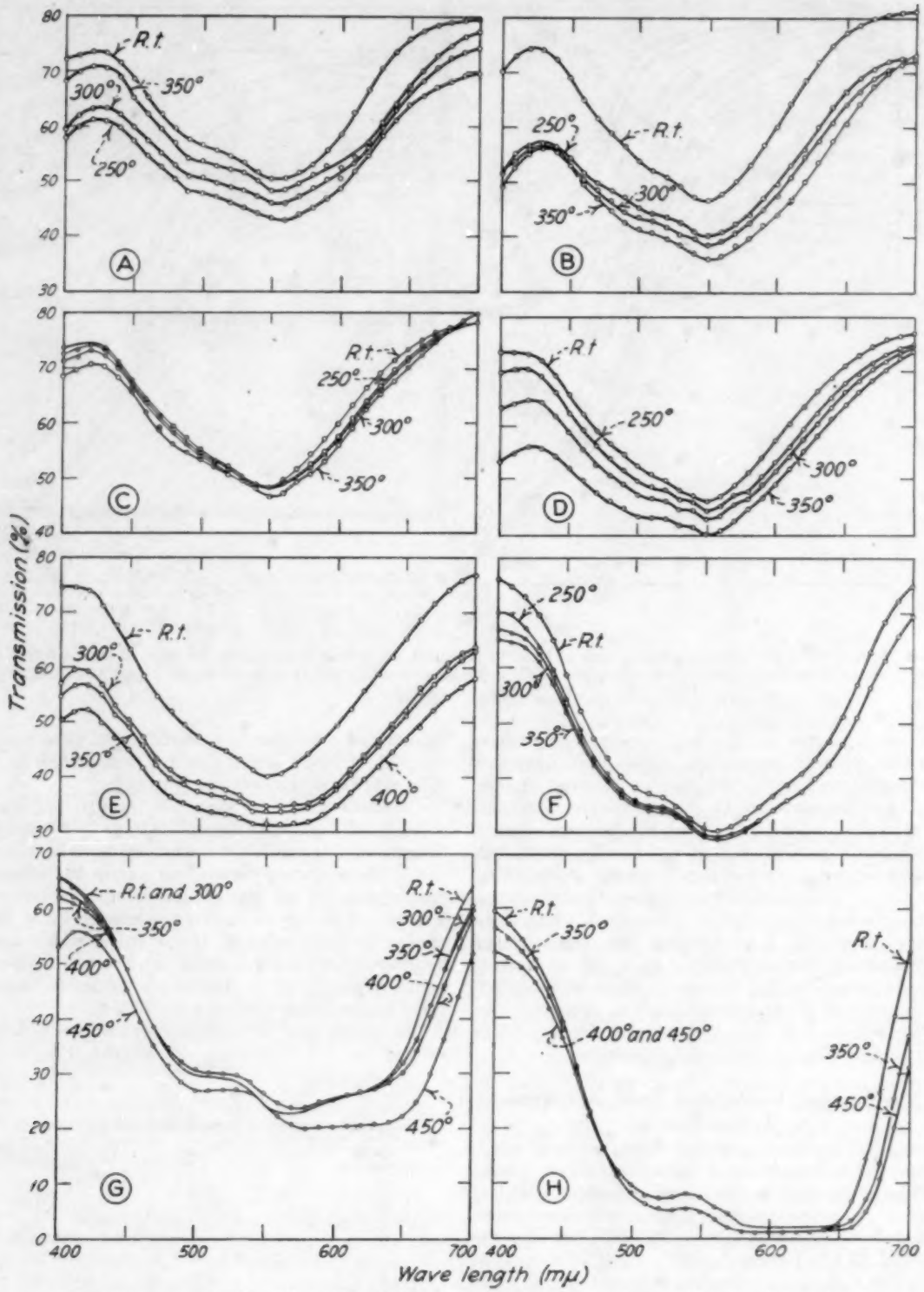
TABLE II

TRANSFORMATION TEMPERATURES OF GLASSES

Glass designation	Temp. (°C.)*	Transformation temp. (°C.)†
A	250	220
B	250	240
C	300	300
D	250	330
E	350	360
F	250	400
G	400	425
H	350	440

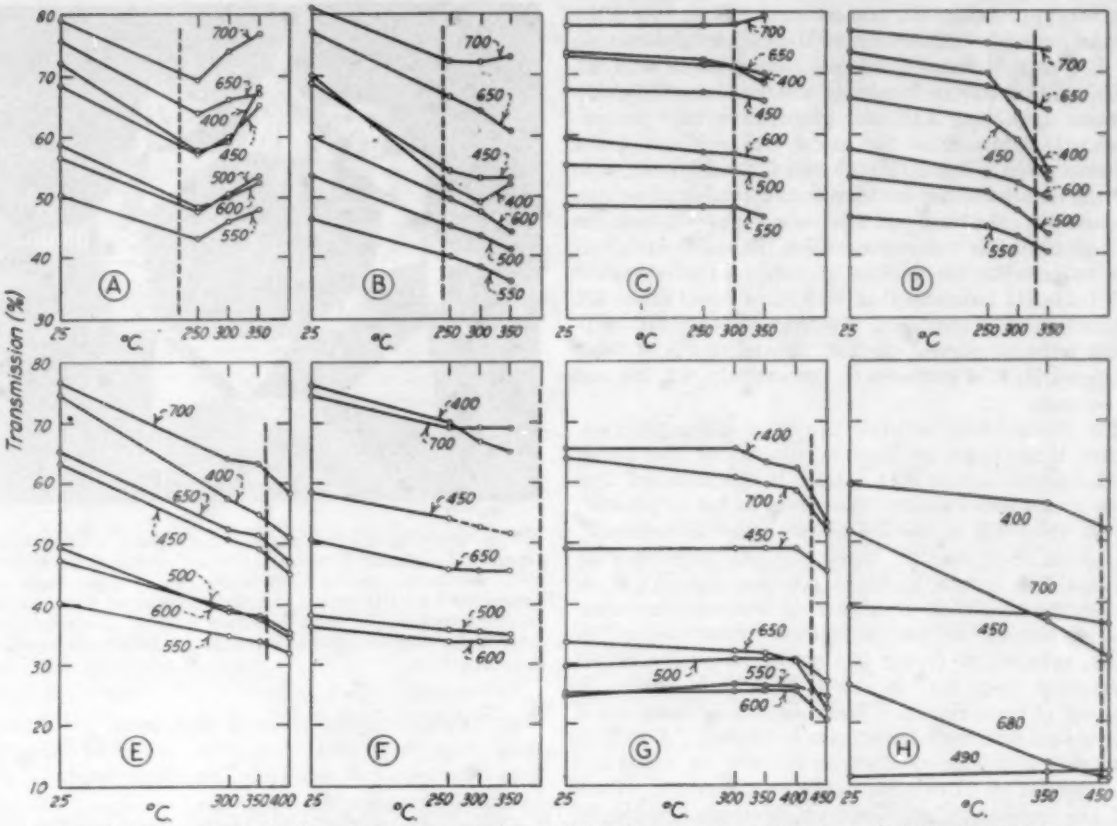
* Indicated by break in curves (Fig. 6).

† E. J. Gooding and W. E. S. Turner, "Study of Series of Glasses Containing Sodium Oxide, Boric Oxide, and Silica," *Jour. Soc. Glass Tech.*, **18**, 32–66T (1934); *Ceram. Abs.*, **13** [9] 234 (1934).



FIGS. 5*A* THROUGH 5*H*.—Spectral transmissions of sodium borate glasses at higher temperatures.

Curve	B_2O_3(%)	Curve	B_2O_3 (%)	Curve	B_2O_3(%)	Curve	B_2O_3(%)
A	100	*C*	90	*E*	85	*G*	80
B	95	*D*	87.5	*F*	82.5	*H*	70



FIGS. 6*A* THROUGH 6*H*.—Percentage transmission of light of constant wave length (mμ) plotted against temperature of glasses given in Fig. 5; vertical broken lines indicate transformation temperatures estimated from data of Gooding and Turner.*

transformation temperatures shown in Fig. 6, as estimated from the data of Gooding and Turner* are shown by the broken vertical lines on each set of curves.

VI. Discussion of Results

X-ray diffraction studies of Biscoe and Warren[4] have shown that boric oxide glass consists of a random network of planar BO_3 units. When soda is added progressively to the boric oxide, there is a tendency for some of the borons to assume tetrahedral coordination. This tendency increases up to about 16% of Na_2O, beyond which it decreases. These authors explain maxima and minima in many physical properties of sodium borate glasses which occur near this percentage of Na_2O to be caused by the tighter structure formed by the increase in number of BO_4 units. The results of the present investigation show that a rapid change in spectral transmission occurred when soda exceeded 10 to 15% of the chemical composition of the glass. The results prove the usefulness of color oxides as indicators of structural changes in glass.

The earlier studies of Brode[5] on alkali-borate glasses containing small amounts of cobalt oxide show that the pink glasses have the same spectral absorption characteristics as those of aqueous solutions of cobaltous salts. Brode's studies also show that the color caused by the cobalt-oxygen coupling is changed because of varying strains in the molecular electrical field surrounding the chromophore, which may be produced by a change in the type of alkali present or by the amount used.

The change in the electrical field surrounding a chromophore may be induced by heat as well as by a change in chemical composition. Klemm and Berger,[6] who used neodymium and praseodymium as coloring indicators, have shown that an abrupt change in spectral transmission occurs at the transformation temperature of the glass. Holland and Turner[7] have provided additional data on changes in transmission of various colored glasses with temperature. The results of the present investigation also indicate that

* See † (dagger) footnote, Table II.

[5] W. R. Brode, "Absorption Spectra of Cobaltous Compounds: IV, Alkali Oxide-Boric Oxide Glasses," *Jour. Amer. Chem. Soc.*, **55** [Part I], 939–47 (1933).

[6] A. Klemm and E. Berger, "Change in Transmission of Glasses with Temperature Below and Above Transformation Point," *Glastech. Ber.*, **14** [6] 194–206 (1936); *Ceram. Abs.*, **16** [7] 200 (1937).

[7] A. J. Holland and W. E. S. Turner, "Investigation into Variation with Temperature on Spectral Transmission of Glasses: I, Transmission in Visual Spectral Region at Temperatures from 20° to Softening Point," *Jour. Soc. Glass Tech.*, **25**, 164–220T (1941); *Ceram. Abs.*, **21** [7] 142 (1942).

an abrupt change in transmission occurs near the transformation temperature of the various glasses.

If a glass is assumed to be a homogeneous array of the various atoms involved, the number of foreign atoms associated with any given atom may be calculated. Thus, from the molar compositions of the glasses given in Table III, columns (2) and (3), the ratio of the number of boron atoms to the number of sodium atoms was calculated and listed in column (4); column (5) gives similar values concerning the ratio of oxygens to sodiums in the various glasses. An examination of Table III indicates that at 10% of Na_2O (glass C), there are approximately 15 oxygens associated with each sodium, whereas at 12.5, 15, and 17.5% of Na_2O (glasses D, E, F), there are, respectively, 12, 10, and 8 oxygens.

In the random network theory of glass structure, there is no exact or fixed orientation of the planar BO_3 units of a pure B_2O_3 glass. If it is assumed that like atoms will separate themselves as far as possible, each boron will be bonded to an oxygen diametrically opposite from another boron. If, furthermore, two planar BO_3 groups having a common corner are assumed to have their planes perpendicular, a maximum oxygen-second oxygen separation would occur. A B_2O_3 network of planar BO_3 units, forming a closed octagonal ring, may be built from these units. If several of these rings are joined in three dimensions, a loose structure with large holes is formed. A sodium ion placed in one of these holes will be uniformly surrounded by 24 oxygens in the B_2O_3 network. Each of the oxygens of the network, however, is equally shared with 3 sodiums giving a net result of 8 network oxygens associated with a sodium in one of these holes.

Biscoe and Warren[4] have shown by X-ray data that each sodium is coordinated with 6 oxygens, which, with the 8 oxygens mentioned, indicates that a sodium ion in one of these holes is surrounded by 14 oxygens. If oxygens are placed between each 2 sodiums, they will be found to exist in the middle of the octagonal rings, thus giving each sodium a coordination of 6. This arrangement assumes that the oxygens in the network are held by the borons and that the excess charge of the oxygen between the sodiums is taken up to give tetrahedral coordination to some of the borons.

Figure 7 illustrates a three-dimensional model of such a glass. Each triangle represents a planar BO_3 unit. Two octagonal rings of such units are shown, these rings (front and back) being joined in space by four BO_3 units. A relatively large hole exists in the center of this assembly.

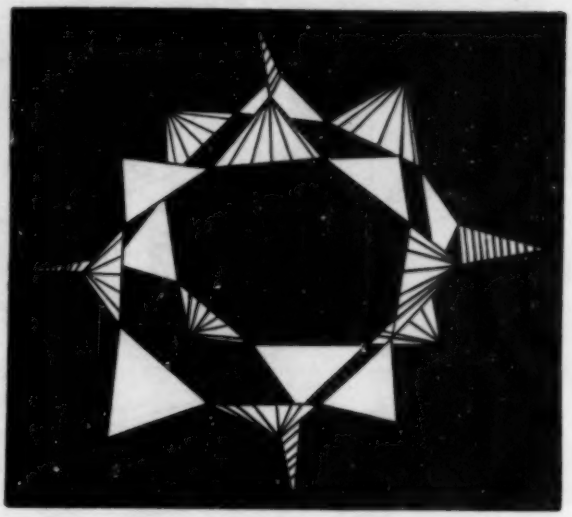


FIG. 7.—Possible space model of B_2O_3 glass; each triangle represents a planar BO_3 unit; two octagonal rings of such units are shown, one in front of the other; these rings are joined by four BO_3 units, the planes being at right angles to one another; in sodium borate glasses, the relatively large holes formed by the assembly of BO_3 units contain sodium atoms.

TABLE III

RELATIVE NUMBERS OF BORON AND OXYGEN ATOMS IN GLASSES WITH RESPECT TO NUMBER OF SODIUM ATOMS

(1)	(2)	(3)	(4)	(5)
A	0	100		
B	4.5	95.5	21.3	32.5
C	9.0	91.0	10.0	15.5
D	11.3	88.7	7.7	12.3
E	13.6	86.4	6.4	10.1
F	15.9	84.1	5.3	8.5
G	18.2	81.8	4.5	7.2
H	27.6	72.4	2.6	4.4

Column Nos.: (1) glass designation; (2) and (3), chemical composition, mol % of Na_2O and of B_2O_3, respectively; (4) ratio of number of B atoms to Na atoms; and (5) ratio of number of O atoms to Na atoms.

Column (5) of Table III shows that glass C (10% of Na_2O *ca.*) comes nearest to fulfilling the conditions for having 14 oxygens associated with each sodium. The transmission versus temperature plot at constant wave length (Fig. 6*C*) shows practically no change of transmission up to the transformation temperature. A similar observation may be made at 20% of Na_2O (Fig. 6*G*). An indication of a stable configuration occurs again at 20% of Na_2O.

If the curves of Figs. 6*A* through 6*H* are examined with reference to increase in soda content of the glasses and to changes in transmission with temperature, a number of inferences may be made.

(1) Pure B_2O_3 glass (Fig. 6*A*) has the characteristics of Brode's[6] cobaltous salts.

(2) Five per cent of Na_2O (Fig. 6*B*) modifies the solution effect as the temperature rises, indicating a high degree of mobility of the sodium ions inasmuch as a marked decrease of transmission occurs below the transformation temperature.

(3) The 10% Na_2O glass (Fig. 6*C*) exhibits a more stable configuration where the holes in the structure are filled and little change of transmission occurs until the transformation temperature is reached.

(4) The glass containing 12.5% of Na_2O (Fig. 6*D*) maintains a low decrease of transmission with temperature increase up to 250°, but a marked decrease of transmission occurs in the blue (short wave lengths) as the temperature is increased above 250°. This change is interpreted to indicate that the number of atoms (Na and O) that are associated with the chromo-

phore exceed those required for stable bonding and that they become active below the transformation temperature.

(5) Figure 6*E* shows the effect of temperature on the 15% Na_2O glass to be a rather marked decrease of transmission from room temperature to the transformation temperature and then a greater rate of decrease with rise in temperature. The action is similar to that of the 12.5% Na_2O glass except that the break in the curve is nearer the transformation temperature.

(6) Figure 6*F* shows an almost linear decrease of transmission with increase of temperature. It is unfortunate that data were not obtained above 350°C.

(7) The glass containing 20% of soda (Fig. 6*G*) acts similarly to that having 10% of soda, indicating possibly that another stable configuration has been reached.

(8) Figure 6*H* shows that the 30% Na_2O glass acts in a similar manner to the 15% Na_2O glass except that at long wave lengths the transmission decreases much more rapidly and produces a change to a purer blue glass.

VII. Conclusions

From the foregoing data and discussion, the following conclusions may be drawn:

(1) An abrupt rate of change of transmissions with temperature occurs at or near the transformation temperature.

(2) The break in property composition curves at about 15% of Na_2O is clearly defined by the transmission curves (Figs. 4*A* and 4*B*).

(3) Sodium borates with approximately 10 and 20% of Na_2O correspond to stable configurations in the glass.

(4) The use of color indicators to note structure changes appears to be a reliable method for studying the structure of glass at high temperatures.

(5) Electrical conductivity data on these glasses at the temperatures used in this study should provide additional information on their structure.

(6) Preliminary experiments with potassium borate glasses indicate similar changes in transmission with temperature to those found for sodium borates.

Acknowledgment

The authors wish to express their appreciation to the Research Board of the Graduate School, the University of Illinois, for funds which helped to defray some of the expenses of this investigation and also to C. W. Parmelee, Head of the Department of Ceramic Engineering, for his encouragement in carrying it out. All measurements of spectral transmission were made by J. O. Kraehenbuehl, Department of Electrical Engineering, by means of a General Electric automatic recording photoelectric spectrophotometer.

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EFFECT OF IRON OXIDE ON PROPERTIES OF SODA-DOLOMITE LIME-SILICA GLASS*

Contribution of the General Research Laboratory, Owens-Illinois Glass Company†

Abstract

In two base glasses, the first containing 16% of sodium oxide, 10% of dolomite lime, and 74% of silica, and the second with 14% of sodium oxide, 12% of dolomite lime, and 74% of silica, iron oxide was systematically substituted for (*a*) Na_2O, (*b*) CaO·MgO, and (*c*) SiO_2 in amounts of 1, 3, and 5%. The effects of these substitutions on such properties as liquidus temperature, viscosity, deformation temperature, fiber softening point, density, coefficient of expansion, and the resistance of the glasses to dilute acid and distilled water, are presented.

I. Introduction

This laboratory has carried out, during the past several years, a number of investigations on the effect of composition on several important physical and chemical properties of that type of glass commonly referred to as "soda lime." Two of the largest series studied have been (*A*), the system Na_2O–CaO·MgO–Al_2O_3–SiO_2, and (*B*), the system Na_2O–CaO–Al_2O_3–SiO_2. The effect of the substitution of BaO and of ZnO for (*a*) SiO_2, (*b*) CaO·MgO and (*c*) Na_2O in one typical soda-dolomite lime-silica glass of series A has already been described.[1]

The present study describes some of the results of the substitution of iron oxide in two soda-dolomite lime-silica glasses.

II. Chemical Composition and Preparation

The raw materials used in the preparation of the glasses were Ottawa sand, burned dolomite, Solvay soda ash, c.p. ferric oxide, and ammonium sulfate.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Glass Division). Received April 23, 1942.

† This work was a cooperative effort under the supervision of C. L. Babcock and W. B. Silverman. The following members of the research staff were responsible for the preparation of glasses, chemical analyses, and measurement of various properties: Paul Close, Frank Bacon, J. F. White, V. C. Rees, J. Miller, and R. C. Kennedy.

[1] Owens-Illinois Glass Company, General Research Laboratory, "Effect of Barium Oxide and Zinc Oxide on Properties of Soda-Dolomite Lime-Silica Glass," *Jour. Amer. Ceram. Soc.*, 25 [Feb. 1, No. 3] 61–68 (1942).

TABLE I

CHEMICAL ANALYSES AND PROPERTIES OF 10% DOLOMITE LIME GLASSES CONTAINING IRON OXIDE

	Glass No.									
	10-0	10-1S	10-3S	10-5S	10-1D	10-3D	10-5D	10-1N	10-3N	10-5N
SiO_2	73.4	72.6	70.7	68.6	73.6	73.6	73.6	73.5	73.5	73.6
R_2O_3	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
CaO	6.1	5.9	5.9	5.9	5.3	4.1	2.9	6.0	5.9	5.9
MgO	4.2	4.1	4.1	4.2	3.7	2.9	2.1	4.1	4.2	4.1
Na_2O	15.8	15.8	15.8	15.9	15.9	15.9	15.9	14.9	13.0	11.1
Fe_2O_3		1.0	2.9	4.9	1.0	2.9	4.9	1.0	3.0	4.8
Total	99.6	99.6	99.6	99.7	99.7	99.6	99.6	99.7	99.8	99.7
Log viscosity (°F.)										
2.00	2685	2680	2600	2540	2690	2690	2750	2700	2740	2875
3.00	2167	2160	2115	2080	2170	2180	2200	2185	2250	2315
4.00	1848	1840	1815	1790	1850	1855	1860	1870	1930	1970
5.00	1634	1620	1605	1590	1630	1630	1625	1650	1705	1730
6.00	1481	1470	1455	1440	1475	1470	1455	1495	1540	1560
7.00	1362	1355	1340	1330	1360	1340	1330	1375	1410	1435
7.65	1301	1295	1280	1270	1295	1275	1260	1310	1340	1365
Liquidus temp. (°F.)*	1670	1560	1700	1820	1670	1730	1710	1850	1870	2060
Coeff. of expansion ($\times 10^7$/°C.)	91	92	94	94	92	92	91	88	83	76
Deformation temp. (°F.)	1035	1025	1023	1022	1030	1024	1018	1045	1065	1082
Chemical durability (% of Na_2O) water	0.073	0.065	0.051	0.038	0.068	0.057	0.055	0.056	0.030	0.016
Chemical durability (% of Na_2O) $N/50$ H_2SO_4	0.054	0.058	0.051	0.048	0.066	0.075	0.083	0.042	0.020	0.013
Density (gm./cc.)	2.4737	2.4920	2.5212	2.5512	2.4775	2.4830	2.4876	2.4827	2.4937	2.4991

* Tridymite is the primary phase at liquidus temperature indicated throughout except for samples Nos. 10–3S and 10–5S; diopside is the primary phase in these samples.

Ammonium sulfate, in an amount sufficient to yield approximately 0.2% of SO_3 in the finished glass, was used as a refining agent in the preparation of all of the glasses. The analyses of the raw materials which introduced small amounts of impurities into the glasses were as follows:

	Burned dolomite (%)	Ottawa sand (%)
SiO_2	0.6	99.7
R_2O_3	0.3	0.2
SO_3	0.6	
CaO	57.2	
MgO	40.1	
Ignition loss	1.2	

Approximately 4.5 lb. of each glass were melted in a large covered platinum crucible in a gas-fired furnace. The glasses were stirred several times during the initial melting period and were poured, crushed, and remelted, with additional stirring. The total time of melting and remelting was approximately 20 hours at approximately 2600°F.

The actual chemical analyses as well as all measured properties of the 10% dolomite lime glasses are shown in Table I, and similar data for the 12% dolomite lime glasses are given in Table II. The first glass in each of these tables, namely, No. 10–0 and No. 12–0, respectively, is the base glass for that particular series.

III. Properties Measured and Methods of Determination

The following properties of the glass were determined: (1) density, (2) liquidus temperature, (3) coefficient of expansion, (4) deformation temperature, (5) viscosity, (*a*) fiber softening point and (*b*) high-temperature viscosity, (6) resistance to dilute acid, and (7) resistance to distilled water.

The methods of determination were exactly the same as those used in the work previously reported.[1]

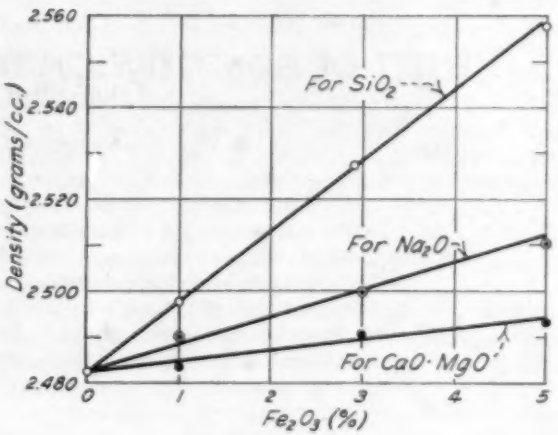

FIG. 1.—Effect of Fe_2O_3 substitutions on density (10% dolomite).

IV. Discussion of Results

The measured data on the twenty glasses are shown in Tables I and II, and Figs. 1 to 19 show in graphical form the effects of the substitutions on the various properties.

TABLE II

CHEMICAL ANALYSES AND PROPERTIES OF 12% DOLOMITE LIME GLASSES CONTAINING IRON OXIDE

	Glass No.									
	12-0	12-1S	12-3S	12-5S	12-1D	12-3D	12-5D	12-1N	12-3N	12-5N
SiO_2	73.6	72.6	70.5	68.6	73.5	73.6	73.6	73.5	73.6	73.7
R_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
CaO	7.1	7.0	7.1	7.1	6.6	5.4	4.2	7.1	7.2	7.1
MgO	4.9	4.9	4.9	5.0	4.5	3.7	2.9	5.0	5.0	5.0
Na_2O	13.9	13.9	14.0	14.0	13.9	13.9	14.0	13.0	11.0	9.0
Fe_2O_3		1.0	2.9	5.0	1.0	3.0	5.0	1.0	3.0	5.0
Total	99.7	99.6	99.6	99.9	99.7	99.8	99.9	99.8	100.0	100.0
Log viscosity (°F.)										
2.00	2665	2690	2610	2580	2700	2740	2770	2730	2770	2880
3.00	2210	2195	2150	2125	2210	2230	2240	2215	2275	2335
4.00	1905	1885	1850	1835	1900	1905	1900	1900	1960	2005
5.00	1690	1670	1650	1635	1680	1680	1670	1685	1740	1780
6.00	1530	1510	1495	1485	1520	1510	1500	1530	1580	1615
7.00	1405	1395	1380	1370	1395	1385	1370	1415	1455	1490
7.65	1340	1330	1320	1310	1330	1315	1300	1355	1390	1425
Liquidus temp. (°F.)*	1840	1840	1850	1870	1840	1800	1850	1870	2020	2250
Coeff. of expansion ($\times 10^7$/°C.)	87	87	89	88	88	86	88	83	79	73
Deformation temp. (°F.)	1064	1061	1058	1060	1057	1050	1043	1075	1095	1128
Chemical durability (% of Na_2O) water	0.058	0.050	0.037	0.029	0.053	0.037	0.032	0.045	0.024	0.012
Chemical durability (% of Na_2O) $N/50$ H_2SO_4	0.028	0.028	0.027	0.024	0.028	0.030	0.033	0.022	0.012	0.008
Density (gm./cc.)	2.4825	2.4977	2.5273	2.5573	2.4826	2.4902	2.4928	2.4904	2.5002	2.5104

* Tridymite is the primary phase at the liquidus temperatures indicated throughout except for samples Nos. 12–1S, 12–3S, and 12–5S; diopside is the primary phase in these samples.

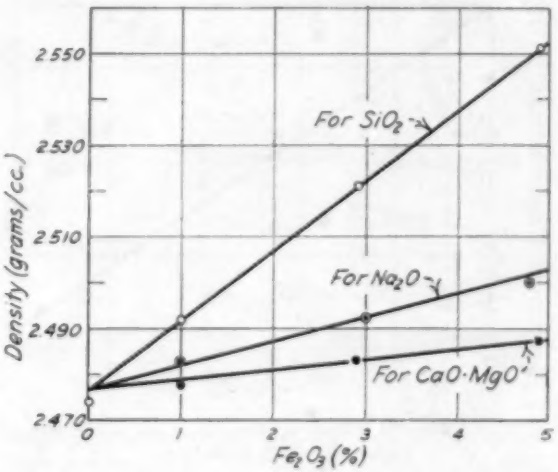

FIG. 2.—Effect of Fe_2O_3 substitutions on density (12% dolomite).

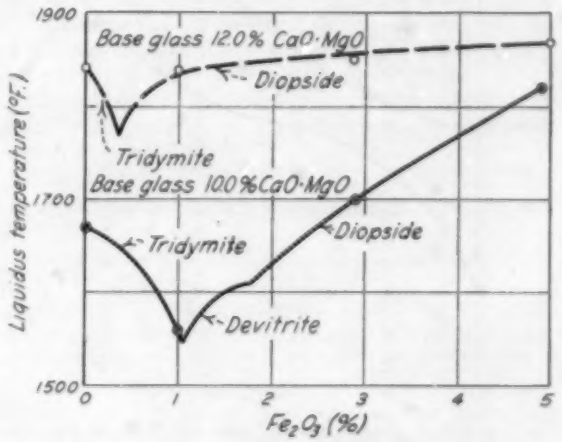

FIG. 3.—Effect of substituting Fe_2O_3 for SiO_2 on liquidus temperature.

(1) Density

(*a*) Figure 1 shows the effect of the substitution of iron oxide on density in the 10% dolomite lime glasses. The substitution of Fe_2O_3 for SiO_2, CaO·MgO, or Na_2O results in an increase in density. The approximate amounts of increase for 1% substitutions for these oxides are, respectively, 0.015, 0.005, and 0.002 gm. per cc.

(*b*) Figure 2 shows the effect of the substitution of iron oxide on density in the 12% dolomite lime glasses. The substitution of Fe_2O_3 for SiO_2, CaO·MgO, or Na_2O results in an increase in density. The approximate amounts of increase for 1% substitutions for these oxides are, respectively, 0.015, 0.006, and 0.002 gm. per cc.

These data show that the effect of adding Fe_2O_3 to these glasses causes an increase in density and that the amounts of such increases are the same for both the 10 and 12% dolomite glasses.

(2) Liquidus Temperature

Figure 3 shows the effect on the liquidus temperature of the substitution of Fe_2O_3 for SiO_2 in the two series of glasses.

The replacement of SiO_2 by Fe_2O_3 in the 10% dolo-

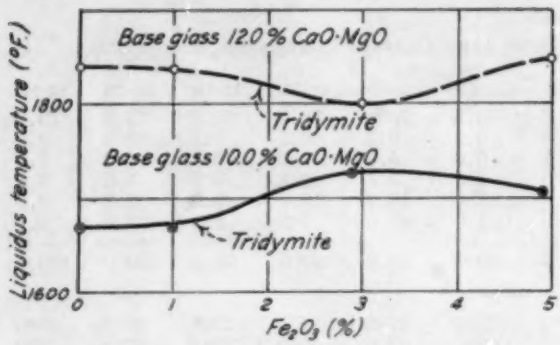

FIG. 4.—Effect of substituting Fe_2O_3 for CaO·MgO on liquidus temperature.

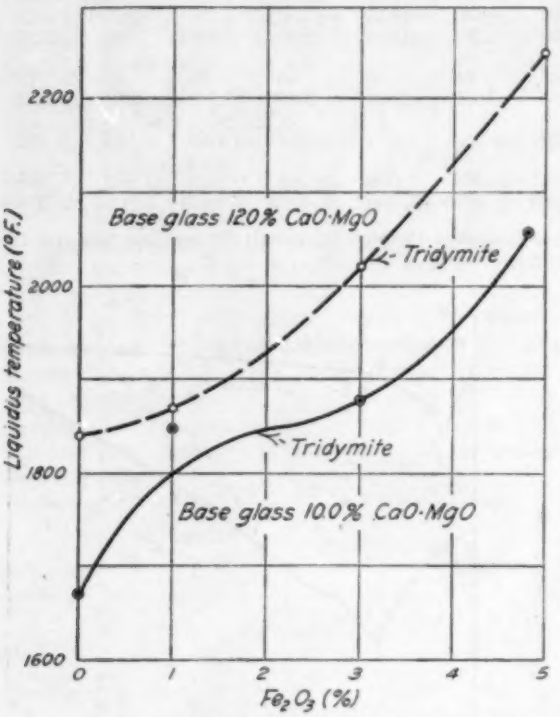

FIG. 5.—Effect of substituting Fe_2O_3 for Na_2O on liquidus temperature.

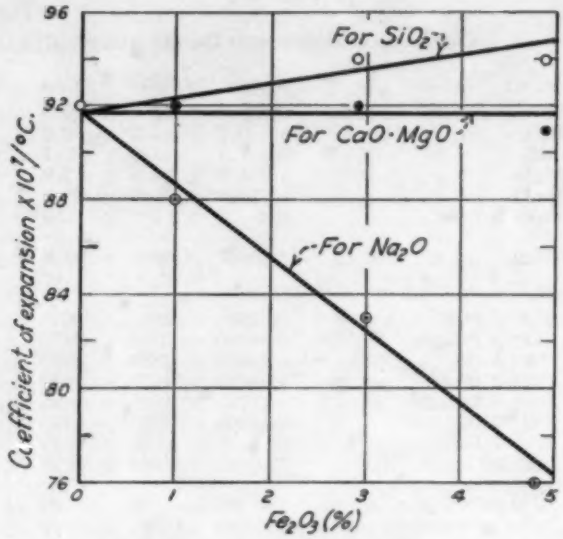

FIG. 6.—Effect of Fe_2O_3 substitutions on coefficient of expansion (10% dolomite).

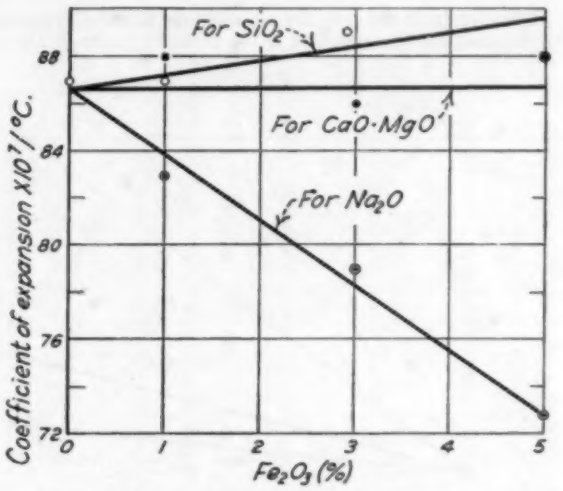

FIG. 7.—Effect of Fe_2O_3 substitutions on coefficient of expansion (12% dolomite).

mite lime glasses causes a very rapid drop in the liquidus temperature up to the boundary line between the tridymite and devitrite fields, which occurs near 1% of Fe_2O_3. Further substitution of Fe_2O_3 up to 5% causes a rapid rise in the liquidus temperature. The boundary line between devitrite and diopside occurs at approximately 1.75% of Fe_2O_3.

The replacement of SiO_2 by Fe_2O_3 in the 12% dolomite glasses causes a very rapid decrease in the liquidus temperature up to the boundary line between tridymite and diopside, which occurs at approximately 0.4% of Fe_2O_3. Further substitution of Fe_2O_3 up to 1% causes a rapid rise in liquidus temperature; substitutions of Fe_2O_3 from 1 to 5% cause slight increases in the liquidus temperatures.

The direction of isotherms and the compositions at which phase changes occur have been determined by blending glasses of known compositions which are not listed in the data shown. All compositions close to these boundary lines are extremely difficult to devitrify.

Strictly speaking, the phase referred to as diopside is really pyroxene, which is a solid solution of diopside containing iron oxide.

Figure 4 shows the effect on the liquidus temperature of the substitution of Fe_2O_3 for CaO·MgO in the 10 and 12% dolomite lime base glasses. Tridymite is the only primary phase which will separate from these glasses.

The replacement of CaO·MgO by Fe_2O_3 in the 10% dolomite series causes no change in the liquidus

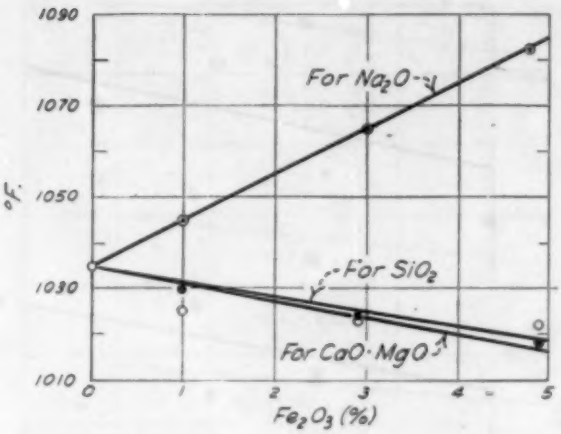

FIG. 8.—Effect of Fe_2O_3 substitutions on deformation temperature (10% dolomite).

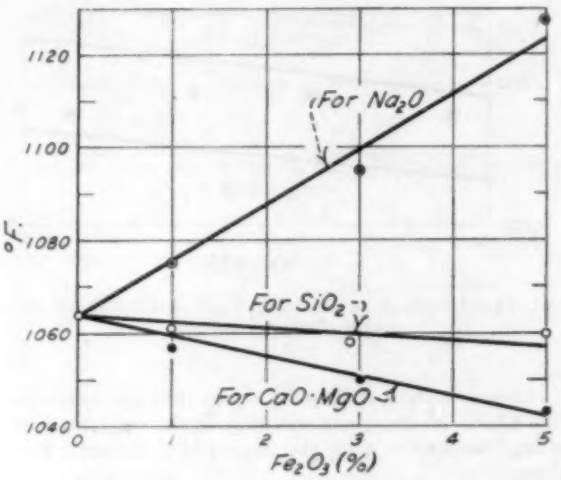

FIG. 9.—Effect of Fe_2O_3 substitutions on deformation temperature (12% dolomite).

temperature in amounts up to 1%, but further substitution causes a slight increase up to about 3%, after which a slight decrease occurs.

The replacement of CaO·MgO by Fe_2O_3 in the 12% dolomite series causes no change in the liquidus temperature in amounts up to 1%. Further substitution, however, causes a slight decrease up to about 3%, after which an increase occurs.

Figure 5 shows the effect on the liquidus temperatures caused by a substitution of Fe_2O_3 for Na_2O. No primary phase other than tridymite will crystallize from this group of glasses. The replacement of Na_2O by Fe_2O_3 results in rapid increases in the liquidus temperatures in both the 10 and 12% dolomite lime glasses.

The data also show that the liquidus temperatures for each of the 12% dolomite glasses are higher than for the 10% dolomite lime glasses for each of the compositions shown.

(1942)

(3) Coefficient of Expansion

Figures 6 and 7 show the effects of substituting Fe_2O_3 for the various oxides on the coefficient of thermal expansion; these values are for the temperature range of 80° to 170°C.

The replacement of SiO_2 by Fe_2O_3 causes equal increases in the expansion coefficients for both the 10% and 12% dolomite lime glasses.

The expansion coefficients remain unchanged when CaO·MgO is replaced by Fe_2O_3 in both series of glasses.

The replacement of Na_2O by Fe_2O_3 results in equal decreases in the expansion coefficients in both series of glasses.

The effect of Fe_2O_3 on the thermal expansion coefficient for these glasses is therefore quite similar to that of CaO·MgO.

(4) Deformation Temperature

Figures 8 and 9 show the effects on deformation temperature caused by the substitution of Fe_2O_3 on the constituent oxides. The term "deformation temperature" is used here to designate the temperature at which glasses cease to expand in the interferometer method for determining the expansion characteristics of a glass.[1]

The replacement of SiO_2 by Fe_2O_3 has a variable effect on the deformation temperature. This substitution in the 10% dolomite lime glasses causes an appreciable lowering of the deformation temperature, whereas no significant change occurs in the 12% dolomite lime glasses.

The replacement of CaO·MgO by Fe_2O_3 results in an appreciable lowering of the deformation temperature in both series of glasses.

The replacement of Na_2O by Fe_2O_3 causes rapid elevation of the deformation temperature in both series of glasses.

(5) Viscosity

Although the actual viscosity curves for the individual glasses are not shown, complete viscosity data are given in Tables I and II.

Figures 10 to 15 show the effects of the various substitutions on the temperature necessary to attain log viscosities of 3 to 7. These data will be discussed on the basis of viscosity at high temperatures (log viscosity = 3) and also at low temperatures (log viscosity = 6).

Figures 10 and 13, showing the replacement of SiO_2 by Fe_2O_3, indicate that such a substitution decreases the viscosity throughout the given range. This decrease at high temperatures, which is the same for both series of glasses, is approximately twice as great as that at low temperatures for both series of glasses.

Figures 11 and 14, showing the replacement of CaO·MgO by Fe_2O_3, indicate that such a substitution increases the high-temperature viscosity equally for both series of glasses as well as equal decreases in the low-temperature viscosity for both series. The increase in high-temperature viscosity, moreover, is numerically equal in degrees to the decrease in the low-temperature viscosity for both series.

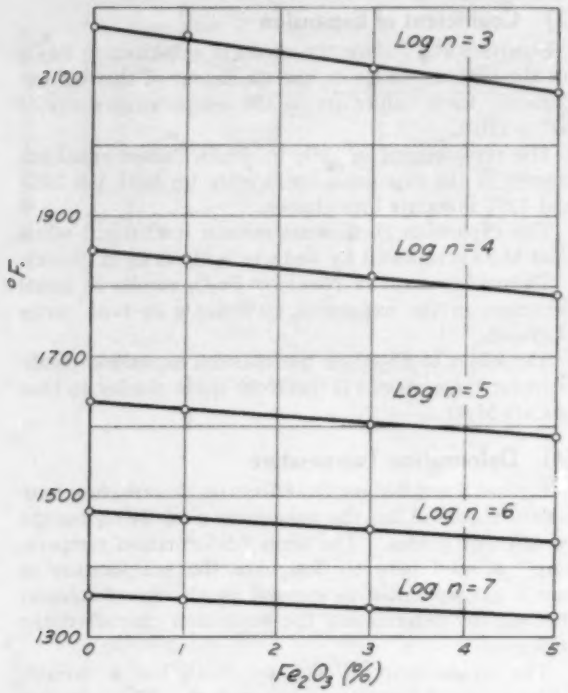

FIG. 10.—Effect of substituting Fe_2O_3 for SiO_2 on viscosity (10% dolomite).

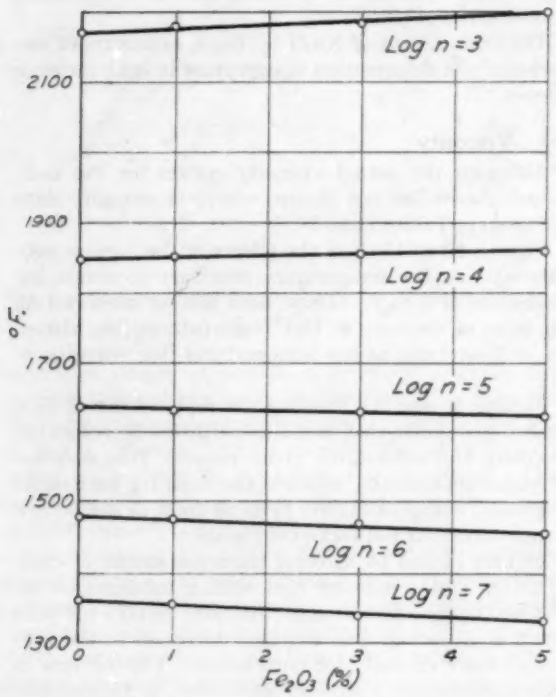

FIG. 11.—Effect of substituting Fe_2O_3 for CaO·MgO on viscosity (10% dolomite).

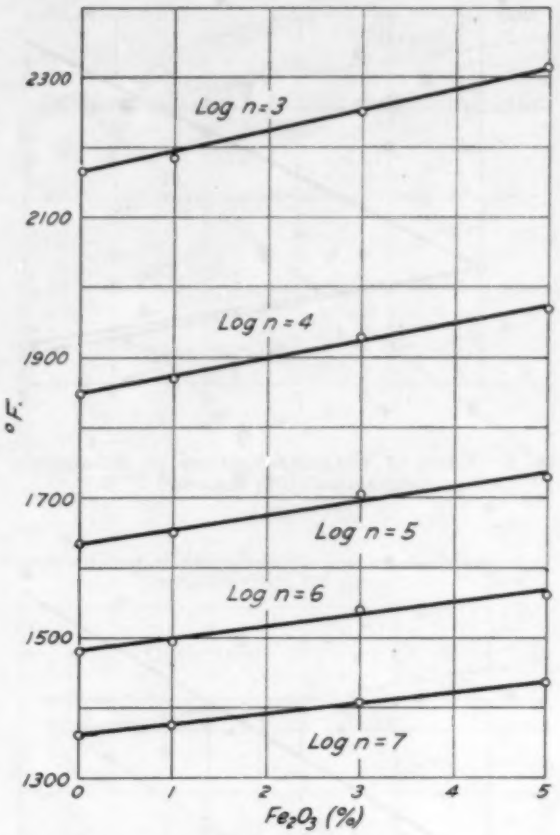

FIG. 12.—Effect of substituting Fe_2O_3 for Na_2O on viscosity (10% dolomite).

An examination of the data shows that this substitution effects no change of viscosity in the neighborhood of log viscosity = 4 for the 10 and 12% dolomite lime glasses.

Figures 12 and 15, showing the replacement of Na_2O by Fe_2O_3, indicate that such a substitution increases the viscosity throughout the range given. This increase in high temperatures in the 10% dolomite series is appreciably greater than that for the 12% dolomite series; at low temperatures, it is approximately the same for both series. The increase at high temperatures, generally speaking, is some one and one-half times as great as the increase at low temperatures for both series.

(6) Resistance to Dilute Acid

Figures 16 and 17 show the effects of the substitution of Fe_2O_3 on the so-called acid durability of both series of glasses. The replacement of SiO_2 by Fe_2O_3 results in a slight increase in the resistance of the glass to dilute acid for both series; the change which results in the 12% dolomite series, however, is not significant.

The replacement of CaO·MgO by Fe_2O_3 causes a definite decrease in dilute acid resistance in the 10% dolomite series, whereas a slight decrease occurs in the 12% dolomite series.

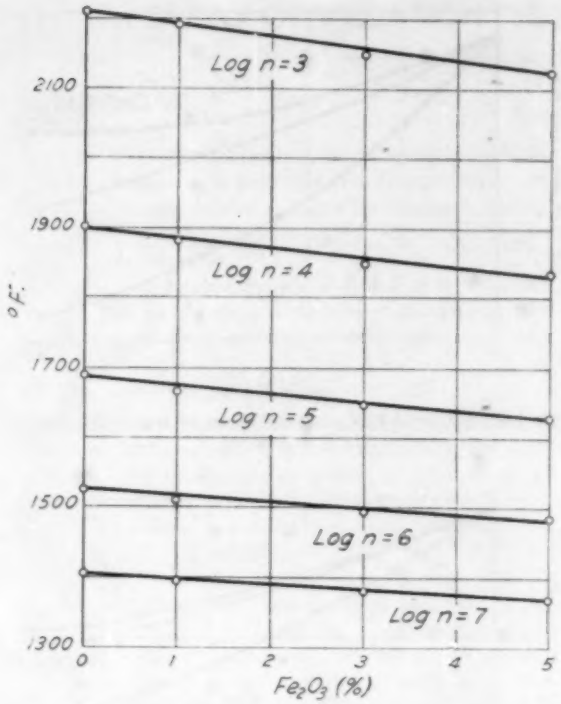

FIG. 13.—Effect of substituting Fe_2O_3 for SiO_2 on viscosity (12% dolomite).

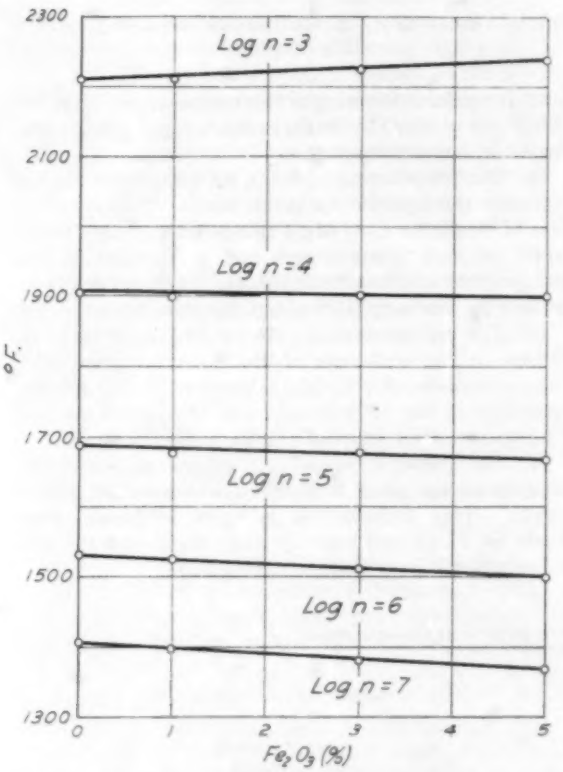

FIG. 14.—Effect of substituting Fe_2O_3 for CaO·MgO on viscosity (12% dolomite).

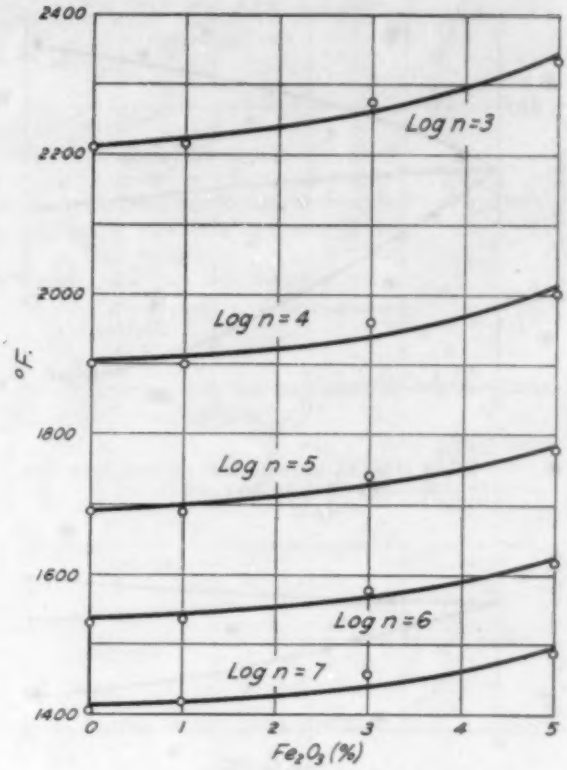

FIG. 15.—Effect of substituting Fe_2O_3 for Na_2O on viscosity (12% dolomite).

The replacement of Na_2O by Fe_2O_3 results in a definite increase in dilute acid resistance, the effect being much more pronounced in the 10% dolomite series.

The changes caused in this property by Fe_2O_3 substitutions are much greater in the 10% dolomite series than in the 12% dolomite series.

(7) Resistance to Distilled Water

Figures 18 and 19 show the effect of the substitution of Fe_2O_3 for the constituent oxides of both series of glasses on resistance of these glasses to distilled water. All of the Fe_2O_3 substitutions result in definite improvement in resistance to distilled water for both series. The replacement of Na_2O by Fe_2O_3 causes the greatest improvement in resistance to distilled water, and the replacement of CaO·MgO by Fe_2O_3 has the least. The replacement of SiO_2 by Fe_2O_3 is intermediate in its effect in both series.

The changes in this property caused by Fe_2O_3 substitutions are greater in the 10% dolomite series than in the 12% dolomite glasses.

V. Conclusions

The following conclusions and observations, which may be drawn from the data presented, are applicable only to the substitution of Fe_2O_3 in the two series described here.

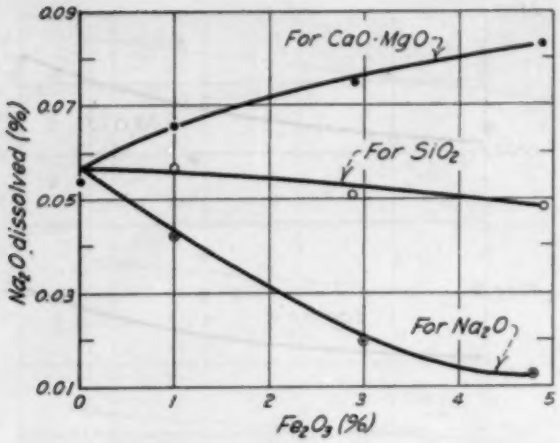

FIG. 16.—Effect of Fe_2O_3 substitutions on acid durability (10% dolomite).

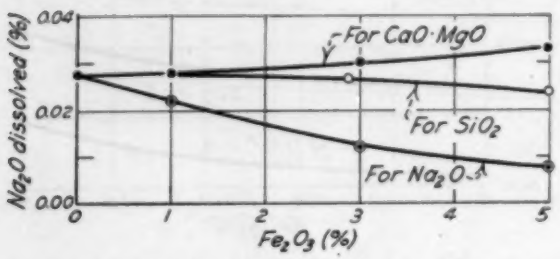

FIG. 17.—Effect of Fe_2O_3 substitutions on acid durability (12% dolomite).

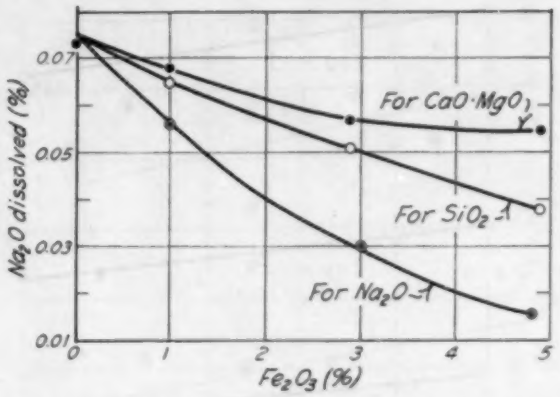

FIG. 18.—Effect of Fe_2O_3 substitutions on water durability (10% dolomite).

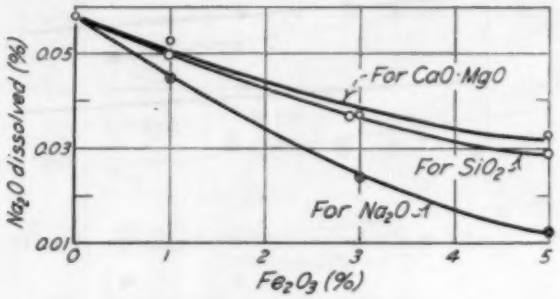

FIG. 19.—Effect of Fe_2O_3 substitutions on water durability (12% dolomite).

(1) The effect of this substitution on increasing the density of the glass is quantitatively the same in both series of glasses.

(2) When substituted for SiO_2, Fe_2O_3 causes at first a lowering of the liquidus temperature and then an increase. When substituted for CaO·MgO, Fe_2O_3 at first causes no change in liquidus temperature and is then different for the two series. When substituted for Na_2O, Fe_2O_3 causes pronounced increases in the liquidus temperature. The Fe_2O_3 substitution, in general, causes the greatest changes when it replaces Na_2O and the least when it replaces CaO·MgO; the SiO_2 replacement has an intermediate effect.

(3) The effects of this substitution on the expansion coefficient of the glass are similar. The replacement of SiO_2 causes an increase in expansion coefficient, replacement of CaO·MgO results in no change, and replacement of Na_2O causes decrease.

(4) The replacement of SiO_2 by Fe_2O_3 has a variable effect on deformation temperature, causing a lowering in the 10% series and no significant change in the 12% series. The replacement of CaO·MgO by Fe_2O_3 results in an appreciable lowering of this temperature. The replacement of Na_2O by Fe_2O_3 causes a rapid elevation of the deformation temperature.

(5) The substitution of Fe_2O_3 for SiO_2 decreases the viscosity throughout the given range. The substitution of Fe_2O_3 for CaO·MgO causes an increase in viscosity at high temperatures and a decrease at low temperatures. The substitution of Fe_2O_3 for Na_2O increases the viscosity throughout the given range.

(6) The replacement of SiO_2 by Fe_2O_3 results in no change in the resistance of the glass to dilute acid; the replacement of CaO·MgO, however, is detrimental, especially in the 10% series; and the replacement of Na_2O is beneficial, especially in the 10% series.

(7) The substitution of Fe_2O_3 is beneficial to the resistance of the glass to distilled water for all glasses shown. This substitution is most beneficial when made for Na_2O and least for CaO·MgO, and the SiO_2 substitution is intermediate in its effect.

OWENS-ILLINOIS GLASS COMPANY
TOLEDO, OHIO

DECAY OF VIBRATION PHENOMENA OF GLASS BARS*

By Joe G. McCann

Abstract

The purpose of this investigation was to correlate the decay of vibration of glass bars with their chemical composition. The moduli of decay of four commercial glasses were determined by a photographic method which employed an oscillograph to provide a graphic representation of the audible tone emitted by the bars when they were set in vibration.

By using bars of identical cross section and different lengths, data were obtained showing the relation of length to modulus of decay. The effect of disannealing on the modulus of decay was also investigated.

I. Introduction

It is customary to evaluate the quality of glassware such as a goblet by setting it in vibration and observing the audible tone produced. A goblet of good quality emits a tone which is pleasing to the ear principally because the vibrations are sustained. If the vibrations die away rapidly, the resultant tone is unmelodic and it is concluded that the glass is of inferior quality.

In the present investigation, a method has been developed for making a quantitative measurement of the degree to which vibrations are sustained. This measurement was made in terms of the modulus of decay which is the time (in seconds) necessary for the amplitude or strength of vibration to decrease to 36.8% of its initial value; (36.8% is the reciprocal of the base of the natural logarithms, e, expressed in per cent).

The work was confined to test specimens in the shape of bars. Four chemical compositions were represented, the variation in composition being mainly in the lead content (Table I). A correlation of tone quality and chemical composition was obtained by comparing the moduli of decay of bars of the same shape but of different composition. To obtain some idea of how the shape of a goblet affects its tone qualities, the moduli of decay of bars of different lengths were compared.

II. Theoretical Considerations

The amplitude of vibration of a bar in free-free vibration in its fundamental mode may be described by equation (1).[1]

$$A = A_0 e^{-kt}. \tag{1}$$

A = amplitude of vibration at any time, t.
A_0 = initial amplitude (amplitude at time, $t = 0$).
e = base of natural logarithms = 2.718.
k = constant determining rate of decrease in A_0.
t = time (seconds).

When $t = 1/k$, $A = A_0/e$.

This "time," called the modulus of decay, and designated by the Greek letter, τ, is the time required for the amplitude of vibration to decrease to 36.8% of its initial value.

If the natural frequency of vibration of the bar is f cycles per second, the bar will execute one complete cycle in a time $1/f$ second, then

$$A_{n+1} = A_n e^{-k/f}. \tag{2}$$

A_n = amplitude of vibration at beginning of cycle.
A_{n+1} = amplitude at end of cycle.

At the end of two complete cycles,

$$A_{n+2} = A_n e^{-2k/f}. \tag{3}$$

Similarly, after r complete cycles the amplitude of vibration will be

$$A_{n+r} = A_n e^{-rk/f}. \tag{4}$$

Rearranging the terms of equation (4),

$$\frac{A_n}{A_{n+r}} = e^{k/f}.$$

$$\frac{rk}{f} = \log_e \frac{A_n}{A_{n+r}}. \tag{5}$$

And finally,

$$\tau = \frac{1}{k} = \frac{r}{f \log_e \frac{A_n}{A_{n+r}}}. \tag{6}$$

τ = modulus of decay.
f = natural frequency of vibration of bar.
A_n = amplitude of vibration at any time, t.
A_{n+r} = amplitude of vibration r cycles later.

Equation (6) makes it possible to determine the modulus of decay by measuring the ratio of two amplitudes of vibration, the number of cycles elapsed between the two amplitudes, and the natural frequency of vibration of the bar.

III. Procedure

(1) Forming Test Bars

The bars were composed of glasses of four different chemical compositions and densities (Table I). The glasses were melted in closed pots, and bars, 1 in. wide by 1/4 in. thick, were formed by pressing in a metal mold. The bars were then uniformly and commercially annealed. To investigate the effect of introducing high strains, one set of bars was later disannealed by heating to 1080°F. for a sufficient time to become stabilized and then cooled in air directly from this temperature. During cooling, the bars were suspended by a fine Chromel wire to insure uniform cooling over the entire sample.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Glass Division). Received April 28, 1942.

[1] P. M. Morse, Vibration and Sound, pp. 18–20. McGraw-Hill Book Company, New York, N. Y., 1936.

TABLE I

CHEMICAL ANALYSES AND DENSITIES OF GLASSES USED

	Type I	Type II	Type III	Type IV
SiO_2	73.4	69.2	63.0	56.0
R_2O_3	1.0	0.1	0.1	0.3
CaO	4.8	7.9	5.4	0.4
MgO	3.4	2.9	1.9	0.3
BaO	0.5			
Na_2O	14.2	13.5	8.0	
K_2O	2.7		5.7	14.6
PbO		6.3	15.7	28.5
Density	2.4601	2.6203	2.7795	3.0627

(2) Obtaining Decay Photographs

In order to insure the internal resistance of the glass to be the principal factor producing damping of the vibrations, the bars were supported on stretched strings at their nodes which, for the fundamental mode, occur at a distance of 0.224 times the length from each end as shown in Fig. 1. When supported in this manner, a minimum of energy is transferred to the supports, and any damping observed may be considered to be characteristic of the glass itself. Each of the two supporting strings was attached to its own metal frame, and the distance between the supports could be adjusted for bars of different length by means of a screw arrangement.

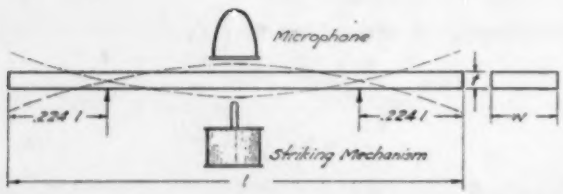

FIG. 1.—Bars supported on stretched strings at their nodes at 0.224 times length from each end for obtaining decay photographs.

The bars were set in vibration by a single tap from a solenoid striking device mounted between the supports and beneath the bar so as to strike it in the center of the under side. A crystal microphone mounted above the center of the bar (not touching it) picked up the sound signal generated by the vibrations. When the signal from the microphone was amplified and impressed on the vertical deflection plates of a cathode-ray oscillograph and the internal sweep frequency of the oscillograph synchronized with the natural frequency of the bar, a graphic representation of the wave form of the sound generated by the vibrating bar was obtained on the oscillograph screen. As nearly as could be judged by eye, the wave form was always that of a damped sine wave, as would be expected.

The amplitude of the sine wave became less as the vibrations of the bar decreased in amplitude. When a study of decay of tone was first suggested,[2] it was thought that a still photograph of the oscillograph screen taken as the decay of vibration was being depicted could be used to obtain qualitative comparisons of the decay of tone by observing the distances between successive traces. A further study of this method proved it to be impracticable for several reasons.

When the internal sweep frequency of the oscillograph was adjusted to be as low as possible,[3] the pattern of the decay of tone of the vibrating bar was that shown in Fig. 2. Three sweeps occurred during the exposure, leaving the three superimposed patterns. Inasmuch as the sweep of the oscillograph provides a horizontal time axis which is superimposed at regular intervals, successive patterns may be shifted to the right to produce a continuous sequence as shown in Fig. 3. It is evident that the decay of vibration is exponential as would be expected. The low sweep frequency used in this instance does not permit the individual waves to be seen, only their envelope. Actually the pattern was produced by a large number of cycles of a damped sine wave as shown in Fig. 4.

Usable patterns, such as the one shown in Fig. 5, were produced by using a somewhat higher sweep frequency (from 10 to 60 cycles per second) and a higher horizontal gain. In Fig. 5, ten sweeps occurred during the time between the opening and closing of the camera shutter, leaving ten pairs of lines of dots. Except for the peak amplitudes, which show up as dots, the sine waves are not distinctly recorded until the vibrations have been considerably damped. Had the camera shutter been left open until the bar ceased to vibrate, many more traces of lower amplitude would have been recorded. Zero amplitude would be represented by a horizontal line in the center of the photograph. Dots lying on or near a vertical line drawn anywhere on the photograph represent amplitudes occurring at intervals of $1/F$ second, where F is the sweep frequency of the oscillograph.

(3) Determining Modulus of Decay

By impressing a known 60-cycle signal instead of the microphone input on the vertical deflection plates and adjusting the sweep frequency until 1, 2, 3, etc., complete waves appeared on the screen, the sweep frequency could be set at 60, 30, 20, etc., cycles per second, respectively. By also applying a 60-cycle signal to the external synchronization terminals, the frequency could be kept from shifting while a number of exposures was made. The number of complete cycles of the vibrating bar elapsed between the recording of two underlying amplitudes is determined by dividing the natural frequency of the bar by the sweep frequency, that is,

$$r = f/F.$$

Substituting this value into equation (6) gives,

$$\tau = \frac{f/F}{f \log_e \frac{A_n}{A_{n+r}}} = \frac{1}{F \log_e \frac{A_n}{A_{n+r}}}. \qquad (7)$$

F = sweep frequency of oscillograph.

$\frac{A_n}{A_{n+r}}$ = avg. of at least 20 determinations of ratio of underlying amplitudes.

[2] C. J. Koenig, "Use of Nepheline Syenite in Sanitary Porcelain," *Jour. Amer. Ceram. Soc.*, **22** [2] 38–46 (1939).

[3] J. F. Rider, The Cathode Ray Tube at Work. Rider, 1935.

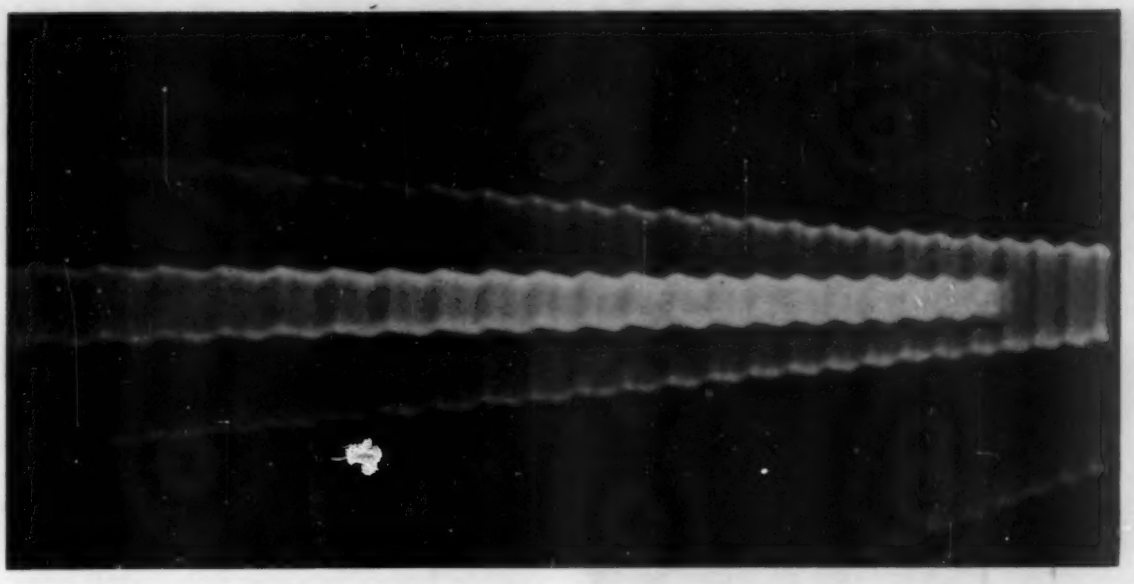

FIG. 2.—Pattern of decay of tone of vibrating bar.

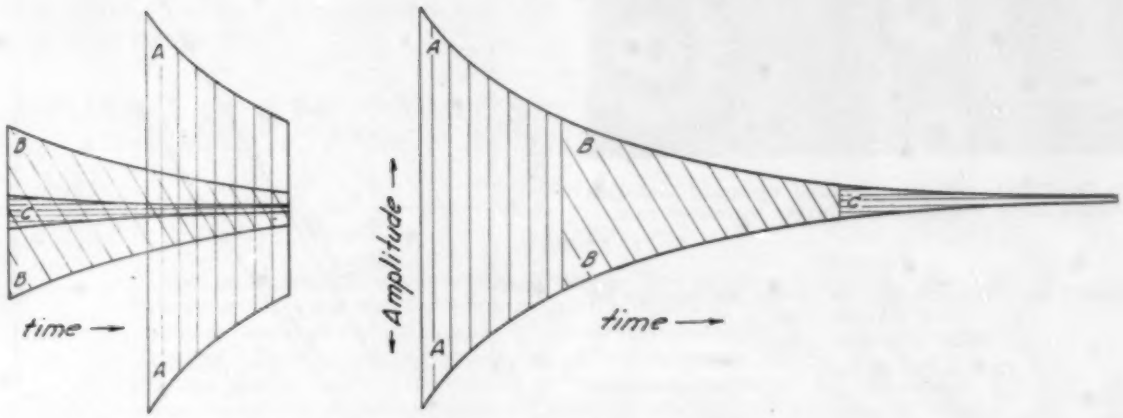

FIG. 3.—Successive patterns of tone decay in continuous sequence.

The photographs were taken with a miniature camera firmly clamped in front of the oscillograph and focused on the screen with an auxiliary lens as shown in Fig. 6. The equipment was adjusted so that the image of the screen completely filled one frame of the 35-mm. film used. A fast emulsion film was necessary to record the rapid fluctuations, and the film was developed for maximum contrast, no attempt being made to secure fine grain. An image of the developed film was projected on a ground glass plate from below with an enlarger. The necessary amplitude measurements were taken from the image appearing on the plate with a vernier calliper, thereby eliminating the necessity of making printed enlargements. In order to estimate the accuracy of the method, the moduli of decay of the bars of type I glass were redetermined. The two sets of results agreed to within about 2.5%. The effects of disannealing on sonic properties are shown in Table II.

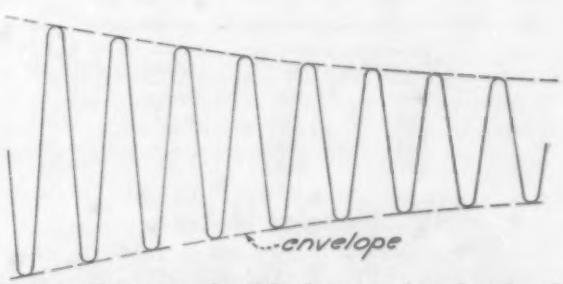

FIG. 4.—Pattern produced by large number of cycles of damped sine wave.

The natural frequency of vibration was determined by the method described by Forgue and Loomis.[4]

[4] S. V. Forgue and G. A. Loomis, "Modulus of Elasticity of Dinnerware Bodies by the Sonic-Vibration Method," *Bull. Amer. Ceram. Soc.*, **20** [12] 425–30 (1941).

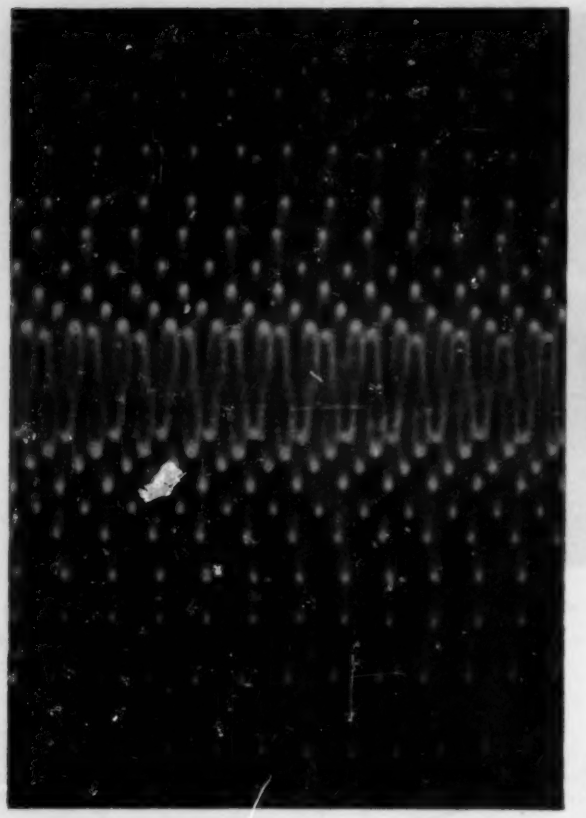

FIG. 5.—Usable patterns produced by using somewhat higher sweep frequency and higher horizontal gain.

TABLE II

EFFECTS OF DISANNEALING ON SONIC PROPERTIES OF TYPE I GLASS BARS

Effect on modulus of decay

Bar length (in.)	Disannealing effect on modulus (sec.)		Modulus decrease	
	Before	After	(sec.)	(%)
5½	0.273	0.196	0.077	28
5	.211	.168	.046	21
4½	.173	.132	.041	24

Effect on fundamental frequency of vibration

	Disannealing effect on frequency (cycles/sec.)		Frequency decrease	
	Before	After	Cycles	(%)
5½	1697	1671	26	1.5
5	2041	2026	15	0.74
4½	2514	2493	21	0.84

IV. Discussion of Results

When the moduli of decay listed in Table III were plotted as shown in Fig. 7, the four solid lines were obtained. Except in the case of the 4-in. bars of type I glass, all of the points fell very nearly on a straight line indicating that the modulus is directly proportional to the length. It must be pointed out, however, that this linearity does not apply to all lengths; for example, when the line representing the type III glass is extended to the left, a negative decay time is indicated for

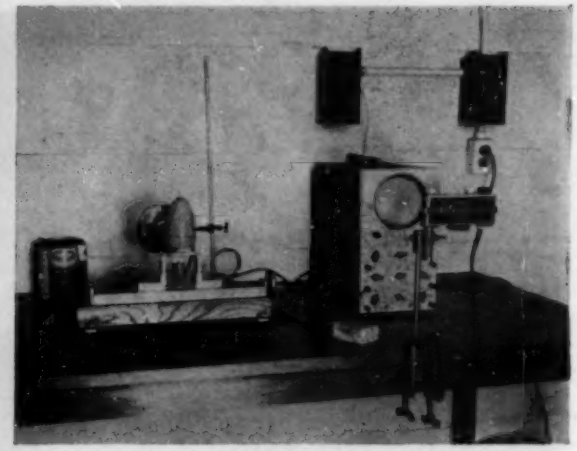

FIG. 6.—Miniature camera clamped in front of oscillograph and focused on screen with auxiliary lens; image of screen completely fills one frame of 35-mm. film.

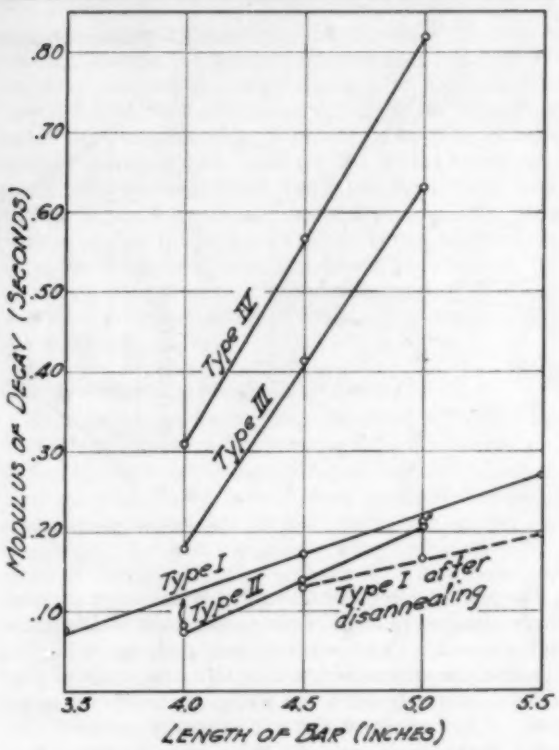

FIG. 7.—Modulus of decay of glass bar sample.

TABLE III

MODULUS OF DECAY OF GLASS BARS

Bar length (in.)	Glass type			
	I	II	III	IV
5½	0.273			
5	.211	0.208	0.632	0.819
4½	.173	.138	.414	.568
4	.0803	.0753	.179	.311
3½	.0764			

a bar whose length is less than 3 in., which of course is impossible. The particular range of lengths tested probably yielded results which fell within the linear range of some more complicated curve; this would account for the apparent discrepancy in the case of the 4-in. type I bars. It may be concluded from Fig. 7 that, as far as tone quality is concerned, type IV glass is superior and types III, I, and II follow in that order. The lead content is apparently the most important factor affecting tone quality as far as chemical composition is concerned. That the lead content is not the only contributing factor is shown by the fact that type I is superior to type II, notwithstanding the fact that type II contains more lead. Also significant is the fact that the higher the lead content of a particular type of glass, the more the modulus of decay is affected by a given change in length. Types I and II are not inverted in this respect. In other words, the tone quality of a goblet of any composition may be improved by altering its design, but the higher the lead content, the greater the improvement will be.

The effect of disannealing is shown in Fig. 7, and it is apparent that this effect is to impair the tone quality.

V. Conclusions

The following conclusions may be drawn from the results of the investigation:

(1) Within the range of lengths tested, the modulus of decay is directly proportional to the length for bars of the same cross section and same chemical composition. This conclusion is significant because it indicates the possibility of improving the tone quality of goblets by altering their design.

(2) For bars of the same length and cross section but of different composition, the high lead content glasses have the best tone qualities.

(3) The slopes of the lines of the graph in Fig. 7 are such that for a given increase in length, the tone qualities of the high lead content glasses are improved more than those of the low lead content.

(4) The effect of disannealing is to lower the pitch of the ring emitted by the vibrating bar and to decrease the length of time the bar continues to ring after it has been set in vibration.

Acknowledgment

The author wishes to express his indebtedness to H. H. Holscher of the Owens-Illinois Glass Company for furnishing the samples, performing the disannealing tests, and offering valuable suggestions. He also wishes to acknowledge the suggestions and advice of G. A. Bole, H. J. Hoffman, and G. A. Loomis.

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INFLUENCE OF FLINT PARTICLE SIZE ON PERMANENT MOISTURE AND THERMAL EXPANSION IN POROUS EARTHENWARE BODIES*

By W. E. Palmer

Abstract

Four progressively finer grain-size distributions of flint were prepared, incorporated in talc-pyrophyllite and clay-flint-feldspar bodies, and fired at cone 9. The permanent moisture expansion, thermal expansion, and crazing resistance of these bodies were determined. Moisture expansion was found to decrease as flint particle size decreased, whereas thermal expansion increased as flint particle size decreased. A pronounced increase occurred in the thermal expansion of talc-pyrophyllite bodies between 100° and 200°C. as flint particle size decreased.

I. Introduction

The importance of flint particle size has long been recognized as a factor in the control of crazing owing to differential thermal expansion between the body and the glaze. Previous investigators have studied the effect of moisture expansion as a cause of crazing,[1] but the relation of flint particle size to moisture expansion has not been reported. The purpose of this investigation was to study the relation of the flint particle size to moisture expansion of talc-pyrophyllite bodies, which were developed by Lintz,[2] and the normal clay-flint-feldspar triaxial body.

The effect of fine-particle flints on thermal expansion in certain types of bodies has also been investigated,[3] and tests of their effect on talc-pyrophyllite bodies have been included in the present study.

II. Materials and Body Composition

Potter's flint, ground from Huntington County,

A thesis presented for professional degree of Ceramic Engineer, Ohio State University, Columbus, Ohio, 1941.

* Received February 5, 1942.

[1] (*a*) H. G. Schurecht and G. R. Pole, "Effect of Water in Expanding Ceramic Bodies of Different Compositions," *Jour. Amer. Ceram. Soc.*, 12 [9] 596–604 (1929).

(*b*) H. H. Holscher, "Expansion of Ceramic Bodies Caused by Liquid and Vapor Penetration," *Ohio State Univ. Eng. Expt. Sta. Circ.*, No. 22, 24 pp. (1931); *Ceram. Abs.*, 16 [2] 68 (1937).

[2] E. H. Lintz, "Use of Talc and Pyrophyllite in Semivitreous Dinnerware Bodies." *Jour. Amer. Ceram. Soc.*, 21 [6] 229–37 (1938).

[3] (*a*) H. Harkort, "Effect of Particle Size of Quartz on Properties of Whiteware Bodies," *Ber. deut. keram. Ges.*, 9 [8] 476–89 (1928); *Ceram. Abs.*, 7 [12] 844 (1928).

(*b*) E. E. Pressler and W. L. Shearer, "Properties of Potter's Flints and Their Effect in Whiteware Bodies," *Bur. Standards Tech. Paper*, No. 310 (1926); p. 306; *Ceram. Abs.*, 5 [11] 368 (1926).

TABLE I

TALC-PYROPHYLLITE AND CLAY-FLINT-FELDSPAR BODIES

	Series A: Talc-pyrophyllite Body No.				Series B: Clay-flint-feldspar Body No.			
	A1	A2	A3	A4	B1	B2	B3	B4
	(%)				(%)			
Bell dark ball clay	18.5	18.5	18.5	18.5	15.1	15.1	15.1	15.1
Bell Dresden ball clay					15.1	15.1	15.1	15.1
Ky. ball clay No. 5	12.5	12.5	12.5	12.5				
Cooley ball clay No. 2	9.0	9.0	9.0	9.0	14.1	14.1	14.1	14.1
Edgar No-Karb Ga. kaolin					5.55	5.55	5.55	5.55
Cherokee Ga. kaolin	10.0	10.0	10.0	10.0				
Harris Lunday N. C. kaolin	10.0	10.0	10.0	10.0				
Kamec N. C. kaolin					5.04	5.04	5.04	5.04
HS pyrophyllite	12.5	12.5	12.5	12.5				
N. C. feldspar	3.5	3.5	3.5	3.5	10.55	10.55	10.55	10.55
Loomis talc	6.0	6.0	6.0	6.0				
Flint	(grain-size distribution)							
No. 1	18.0				34.5			
No. 2		18.0				34.5		
No. 3			18.0				34.5	
No. 4				18.0				34.5

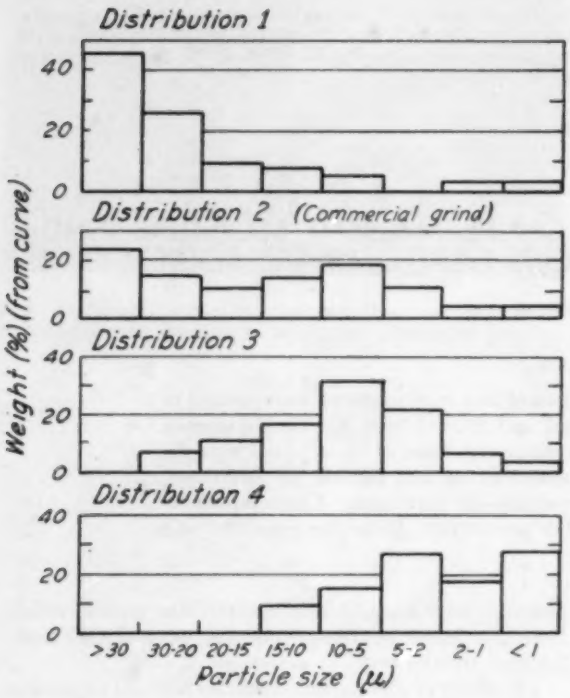

FIG. 1.—Particle-size distribution of flints.

Pennsylvania, quartz sandstone, was elutriated into four portions, and the finest portion was recovered by filter pressing. Equivalent grain-size distribution curves were then determined (Fig. 1).

Two series of bodies were prepared, (*A*) a talc-pyrophyllite series and (*B*) a clay-flint-feldspar triaxial series, incorporating the different flint grain-size fractions as the single varying component. The body compositions, on batch dry weight basis, are given in Table I.

III. Preparation of Specimens and Tests

Each series was batched completely at one time to avoid any variation in the standard ingredients. The bodies were prepared as casting slip with a constant water and electrolyte content. Both types of specimens were cast solid, at a specific gravity of 1.72, in rods $^1/_2$ by 7 in. and in tile $2^1/_4$ by 4 by $^3/_8$ in. The rods were ground to a length of 6 in. for the thermal-expansion tests. Absorption, crazing resistance, and moisture expansion values were determined on the tile specimens. All specimens were fired together in a tunnel kiln to cone 9^2 in 36 hr. Cones, which were placed inside the sagger, showed cone 7^2 (nominally 1200°C.).

(1) Moisture Expansion

Moisture-expansion determinations were made on an apparatus similar to that used at the Ohio State University Engineering Experiment Station,[4] using an Ames dial graduated in ten-thousandths of an inch. The specimens were soaked for 48 hr. in water at room temperature before they were tested; the same specimens were then dried at room temperature, autoclaved over water at 150 lb. of steam pressure, and again measured.

(2) Thermal Expansion

The thermal expansion of the specimens was determined with an apparatus designed at the Bureau of Standards,[5] using a temperature rise of 150°C. per hr.

(3) Crazing Tests

Crazing tests were made in an autoclave over water at the various steam pressures and cycles noted in Table II. A duplicate set of specimens was placed in a dry oven and given the same temperature cycles to check the effect of thermal expansion versus moisture expansion as a cause of crazing.

[4] C. J. Koenig, "Nepheline Syenite in Ceramic Ware," *Ohio State Univ. Eng. Expt. Sta. Bull.*, No. 103, 74 pp. (1939); p. 37; *Ceram. Abs.*, 19 [7] 167 (1940).

[5] American Ceramic Society, Standards Report, *Jour. Amer. Ceram. Soc.*, 11 [6] 522–24 (1928).

TABLE II

MOISTURE EXPANSION

Body	Absorption (%)	Expansion (%)	
		Soak 48 hr. at room temp.	Autoclave 3 hr. at 150 lb./sq. in.
A1	7.38	0.016	0.079
A2	6.46	0.012	0.077
A3	7.65	0.012	0.077
A4	6.67	0.009	0.071
B1	10.8	0.021	0.156
B2	9.28	0.018	0.154
B3	10.24	0.018	0.147
B4	9.9	0.012	0.136

TABLE III

CUMULATIVE CRAZING TESTS

Body No.	At 100 lb./sq. in.			150 lb./sq. in. 3 hr.
	½ hr.	1 hr.	4½ hr.	
A1	None	None	None	Slight
A2	"	"	"	"
A3	"	"	"	None
A4	"	"	"	"
B1	Severe	Extremely severe	Extremely severe	Extremely severe
B2	Slight	Severe	Severe	Severe
B3	None	None	None	Slight
B4	"	"	"	None

The test results on autoclave crazing given in Table III follow closely those for moisture expansion in Table II. All specimens in each member of the series failed simultaneously.

The glaze formula for all of the specimens used was as follows:

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ Na_2O\\0.44\ CaO\\0.35\ PbO\end{matrix}\right\}\ 0.298\ Al_2O_3\ \left\{\begin{matrix}2.95\ SiO_2\\0.291\ B_2O_3\end{matrix}\right.$$

IV. Results and Discussion

(1) Moisture Expansion and Crazing Resistance

The moisture-expansion measurements given in Table II indicate a definite reduction of permanent moisture expansion when the flint particle size is reduced. The percentage of reduction is greater in specimens soaked 48 hr. in water than in those autoclaved 3 hr. at 150 lb. per sq. in. It is interesting to note that the moisture expansion is not a function of absorption. Grain-size distributions 1 (bodies A1 and B1) and 3 (bodies A3 and B3) give higher absorptions than distributions 2 (bodies A2 and B2) and 4 (bodies A4 and B4). Close packing, as determined by the grain-size distribution, no doubt affects the porosity determinations of these bodies.[6]

The duplicate specimens that were subjected to the same temperature cycles in a dry oven showed no crazing as a result of thermal expansion.

[6] C. W. Parmelee and W. R. Morgan, "Effect of Fineness of Flint on Vitrification of a Ceramic Body," *Ceram. Ind.*, **22** [3] 146–52 (1934); *Ceram. Abs.*, **13** [5] 125 (1934).

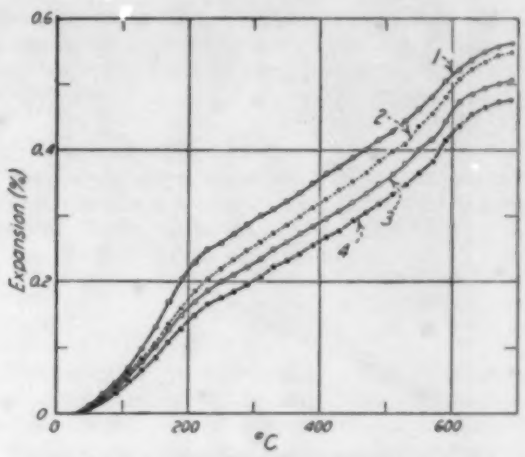

FIG. 2.—Thermal-expansion curves for series A (talc-pyrophyllite); *curve 1*, body A4; *curve 2*, body A3; *curve 3*, body A2; *curve 4*, body A1.

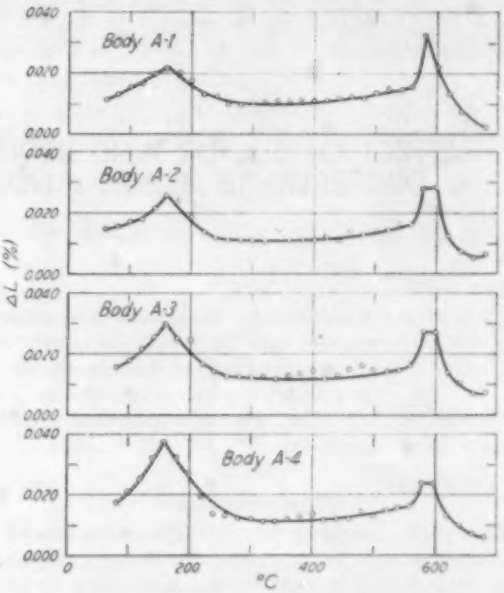

FIG. 3.—Rate-of-change curves of series A bodies, incorporating flints of varying particle-size distribution (readings at intervals of 20°).

(2) Thermal Expansion

(*A*) *Series A, Talc Pyrophyllite:* Series A shows increasing total linear thermal expansion with decreasing particle size (Fig. 2). The range of 100° to 250°C. shows rapid expansion, indicating the presence of forms of silica other than quartz.

The expansions for series A have been replotted (Fig. 3) as rate-of-change curves to show the percentage of change per 20°C. temperature rise. It is interesting to note that the low-temperature inversion is tremendously affected by the particle size of the flint; this reaction is important because glazed bodies are sometimes subjected to service at these temperatures.

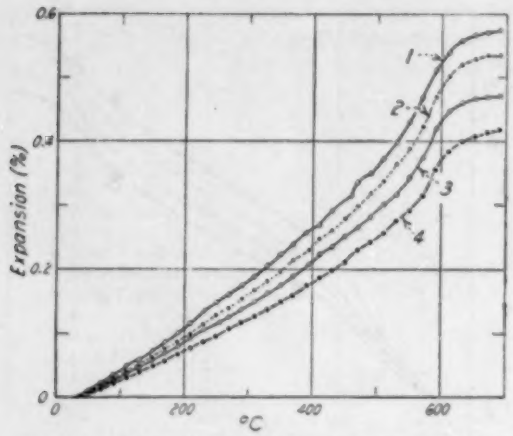

FIG. 4.—Thermal-expansion curves, series B (clay-flint-feldspar); *curve 1*, body B4; *curve 2*, body B3; *curve 3*, body B2; *curve 4*, body B1.

Body A1 (coarse flint distribution) has a low rate of expansion at the interval of 150° to 170°C. and a high rate at 570° to 590°C.; the reverse is true of body A4. This large expansion at 150° to 170°C., lacking other evidence, would necessarily be interpreted to be the result of the presence of tridymite. The shape of the curve suggests that both tridymite and cristobalite are present.

(*B*) *Series B, Clay-Flint-Feldspar:* Series B shows progressively higher thermal-expansion values (Fig. 4) when the particle size of flint is reduced; there is also slight evidence of increased expansion in the cristobalite inversion range for the finest distribution. This fact is well known,[3(b)] but it is repeated here as an interesting contrast to series A to illustrate the effect of body composition.

V. Conclusions

The conclusions drawn from these studies show (1) that in bodies of identical composition and manipulation, definitely lower moisture expansions are obtained as flint particle size decreases and (2) that the yield of forms of silica having inversions below 250°C. is greatly affected by the body composition and flint particle-size distribution. The greatest expansion occurs in the talc-pyrophyllite body with fine flint particle content.

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EFFECT OF SULFUR AND REDUCING GASES ON A SEMIVITREOUS DINNERWARE GLAZE AND DECALCOMANIA DECORATION*

BY I. J. W. MACHATTIE AND A. E. R. WESTMAN†

ABSTRACT

A description is given of difficulties encountered in a pottery manufacturing semivitreous ware following a change-over from natural to manufactured gas. Laboratory investigations showed that exposure to traces of reducing gases for very short periods in the glost firing produced blistered ware and that decalcomania decoration was given a mat appearance when it was exposed to traces of sulfur compounds in the range of 1200° to 1600°F.

I. Introduction

This paper discusses two difficulties encountered in the manufacture of semivitreous dinnerware which followed a change of fuel from natural to manufactured gas in order to conserve natural gas for war industries.

The first defect was the blistering of the glaze of a large proportion of the hollow ware set "in the open," that is, on top of the saggers in the open-fire, circular, glost tunnel kiln. The second was the production of decalcomania decoration, which had a decided mat appearance and a rough feel, from the circular, muffle decorating tunnel kiln. Neither of these difficulties, however, was encountered immediately after changing the glost and decorating kilns to manufactured gas. The defects developed gradually in a three-month period and continued to appear at intervals during the next four months. It was demonstrated several times during this period that reversion to natural gas would immediately cure either defect, and this solution was adopted during periods when natural gas was made available.

Both types of defects (for some reason still not fully understood) tended to appear at the same time; for example, both appeared immediately after the bisque-ware firing was changed from four upright kilns using natural gas to a tunnel kiln fired with manufactured gas.

Apart from this circumstance, however, the difficulties were of quite different character, and they will be discussed separately after the plant background common to both has been reviewed.

(1) Comparison of Natural and Manufactured Gas

Table I gives typical analyses and calculated combustion products of the manufactured and natural gas used at the pottery. It also includes the gas which was used in some of the laboratory experiments to be described later. The manufactured gas was a mixed

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942 (White Wares Division). Received April 19, 1942.

† Mr. MacHattie is Research Fellow in Gas, and Dr. Westman is Director of Chemical Research, Ontario Research Foundation.

coke-oven and carburetted water gas; the laboratory gas was a mixture of coal gas and carburetted water gas. The analyses were made by standard methods, and the sulfur contents were determined by the referees' apparatus.

TABLE I

FUEL GAS ANALYSES AND CALCULATED COMBUSTION PRODUCTS WITH THEORETICAL AIR SUPPLY

Constituent	Natural	Manufactured	Laboratory
Fuel gas analyses	**Types of gases (vol. %)**		
Carbon dioxide	0.2	5.0	2.9
Illuminants*	0.0	4.7	3.7
Oxygen	0.5	0.5	1.9
Hydrogen		62.0	40.5
Carbon monoxide		4.3	15.3
Nitrogen	5.9	3.8	15.0
Methane	89.5	19.7	20.5
Ethane	3.9		0.2
Sulfur (grains/100 cu. ft.)	1	6	13
Calculated composition of combustion products with theoretical air supply (vol. %)			
Carbon dioxide	9.6	9.0	11.0
Nitrogen	71.7	69.6	70.3
Water vapor	18.7	21.4	18.7
Sulfur dioxide (p.p.m. at 60°F. moisture condensed)	2.0	24	55

* For the purpose of calculation, illuminants are assumed to consist of benzene and ethylene in 1-to-1 ratio.

The natural gas differed mainly from the manufactured gas in having a lower sulfur content and a much lower ignition velocity. It contained less moisture as received at the pottery, but calculations showed that this characteristic would not materially influence the percentage of water vapor in the combustion products.

(2) Sulfur Content of Kiln Gases

In determining the sulfur content of kiln gases in the plant and laboratory, a sample of the gas was drawn from a fused silica sampling tube with a glass-wool filter through a fritted glass disperser in an absorption bottle containing an alkaline peroxide solution (*N*/5 NaOH containing 0.15% of H_2O_2) and then through a wet test meter; the suction was provided by a vacuum pump. The absorbed sulfur compounds were precipitated and weighed as barium sulfate and calculated as sulfur dioxide.

This method was adopted in preference to the more usual and convenient methods, based on titration of the absorbing solution, because at least one of these methods was found to be unreliable, presumably the result of interference by nitric oxide. (No time was available to investigate other methods.)

There are necessary precautions in sampling commercial kiln gases. For example, a cork was inserted in the end of the fused silica sampling tube before it was inserted into the furnace and was blown out when the tube was in position. This prevented the kiln dust that adhered loosely to the refractories from entering the tube. Such dust may have a very high sulfur content. When the tube was in position, kiln gases were drawn through it at a steady rate in order to prevent the condensation of moisture near its outlet. A dummy absorption bottle was used when a determination was not being made.

(3) Plant Operation

The percentage of ingredients in the body batch in use at the plant during investigations was American ball clay 30, flint 34, feldspar 11, and kaolin 25%.

The glaze formula was as follows:

$$\left.\begin{matrix}0.18\ KNaO\\0.48\ CaO\\0.34\ PbO\end{matrix}\right\}\ 0.26\ Al_2O_3\ \left\{\begin{matrix}0.37\ B_2O_3\\2.70\ SiO_2\end{matrix}\right.$$

Several other glazes commonly used in American potteries were tried during this period, and they gave identical results as far as defective ware was concerned.

An analysis of the glaze and body showed that both were substantially free from sulfur as they entered the glost kiln.

The bisque ware was fired to 2115° F. on a 55-hour cycle; the glost ware to 1910°F. on a 28-hour cycle; and the decalcomania to 1370°F., with natural gas and to 1400°F. with manufactured gas on an 8-hour cycle.

(4) Investigation of Bisque Kiln

During most of the investigation, the bisque ware was fired in saggers in an open-fire tunnel kiln using manufactured gas.

An analysis of the kiln gases just before the point of high fire showed a sulfur dioxide content of 26 p.p.m., which was about 50% higher than that calculated from the carbon dioxide content and from the analysis of the manufactured gas. This high SO_2 content might have been due to sulfur contributed by the ware or to the formation of a "sulfur eddy" as the ware approached the hot zone, first absorbing sulfur dioxide and later giving it out.

Analyses showed that the unfired ware contained 0.05% of sulfur and the fired bisque 0.01% of sulfur.

II. Glaze Defect

(1) Characteristics

The glaze defect consisted of blistering or bubbling of the glaze which varied in intensity from a few small bubbles near the rim of a piece to a decided blistering, covering one half or more of a piece and leaving craters sometimes 1/8 in. in diameter. It was found on hollow ware, which was set on top of the saggers, and also on flat ware which was exposed locally to the kiln gases by sagger cracks. The blistered portions of the glaze did not differ materially in color from the remainder.

It was assumed at first, from experiments made by Watts,[1] that the blistering was the result of insufficient oxygen in the kiln gases, and this defect was cured on several occasions by making changes in damper settings, which increased the oxygen content of the kiln atmosphere. Much more excess air was required in all cases to avoid this defect when manufactured gas was used.

[1] A. P. Watts, "Effect of Furnace Atmospheres on Quality of Certain Types of Glazes," *Jour. Amer. Ceram. Soc.*, **14** [6] 460–68 (1931).

Although the reason was not always apparent at the time, the appearance of this defect was found sooner or later to be associated with some change that reduced the amount of excess air entering the kiln. Even the firing of the new bisque kiln, referred to earlier, reacted in this way owing to changes in the waste-heat duct system.

(2) Explanations

The experience of the plant operators and a review of the literature suggested several possible explanations, including (1) moisture in the ware, (2) moisture in the kiln gases, (3) sulfur in the kiln gases, (4) the breaking down of sulfates that were introduced with the bisque ware or with the glaze materials or those formed earlier in the glost firing, (5) insufficient oxygen in the kiln atmosphere, and (6) flame impingement.

The experiments of Watts[1] pointed to the fifth explanation as the most probable, although the oxygen content was about 8% and above the 5% limit which he set. Several authors, including Watts, mention blistering caused by flame impingement, but an examination of the kiln showed no visible evidence of flame impingement. The marked effect of hydrogen on enamel glasses, however, which was reported by Geisinger and Berlinghof,[2] was kept in mind when the laboratory investigation was planned.

An analysis showed that the kiln gases had the sulfur content to be expected from the analysis of the gas, that is, 16 p.p.m. as SO_2 and much below the limit set by Watts. It was also shown that explanations (1) and (2) did not apply and that practically no sulfur was introduced by the bisque or glaze materials. One unexpected result was the high sulfur content of dust formed by the sagger wash which collected at ports in the kiln. This dust analyzed 10% of sulfur by weight.

(3) Laboratory Investigation

The laboratory investigation was planned to reproduce the defect under controlled conditions and to reduce further the number of possible explanations.

Arrangements were made to glost fire small pieces of ware in an electrically heated tube furnace through which were passed the products of combustion from a small burner operating on laboratory gas. This gas, as shown in Table I, contained appreciable quantities of sulfur. The nature of the atmosphere so provided could be varied by changing the ratio of air to gas and by adding sulfur dioxide from a cylinder.

The sulfur and sulfate theories did not apply under oxidizing conditions, inasmuch as ware could be fired successfully in atmospheres containing 70 times the sulfur content of the glost kiln atmosphere with the limit ranging between 0.1 and 1% of sulfur dioxide. The addition of sulfuric acid to the unfired glaze did not produce defective ware, nor did a sudden change in oxygen content such as is experienced in the kiln.

It was found, however, that the defect could be produced consistently by subjecting the glaze to slightly reducing conditions at high fire for 15 minutes and then reoxidizing it to remove any discoloration, and it was evident that small amounts of carbon monoxide or hydrogen were responsible for the difficulty.

The data in Table II show that a small change in the air-gas ratio near the neutral point has a marked effect on the appearance of the glaze under conditions of the present experiments. The glazes were exposed to the conditions shown for 15 minutes and then to oxidizing conditions at the same temperature (1150°C., 2100°F.).

TABLE II

EFFECT OF AIR-GAS RATIO ON GLAZE APPEARANCE

Air-gas ratio	Glaze appearance
4.56	Good
4.35	"
4.30	"
4.21*	"
4.14	Full of small bubbles
3.91	Dirty, very rough and bubbly
3.62	" " " " "

* Neutral point, 14.2% of CO_2 in combustion products.

From the rate of movement of the ware in the kiln, it was calculated that one burner in the kiln producing small amounts of hydrogen and carbon monoxide would be sufficient to produce a steady stream of defective ware.

(4) Conclusions

It was concluded that the defective glostware was the result of one or more burners in the kiln allowing small amounts of hydrogen and carbon monoxide to come in contact with the ware. This effect apparently could occur without visible flame impingement, and it was apt to occur with manufactured gas unless sufficient secondary air was drawn into the kiln.

It might be thought that natural gas, being slower burning, would give more difficulty than manufactured gas, but the reverse was true in the plant. (This aspect of the problem awaits solution.) Natural gas may possibly produce carbon monoxide and hydrogen beyond the visible flame, or these gases may be more deleterious when sulfur is present. Ortman's suggestion[3] that reducing gases effect the breakdown of sulfates formed at lower temperatures is interesting in this connection, and it will be investigated in later experiments.

III. The Decoration Defect

(1) Characteristics

The defective decoration was characterized by a mat appearance and a roughness not unlike that of underfired ware. Under the binocular microscope, the decoration appeared to have fused, but it had not united with the glaze to form a common surface as it does with normal ware. The defect was most marked in the top plate of a stack of plates coming from the kiln, and it was progressively less apparent the lower the position of a plate in the stack. Different colors in a decalcomania pattern were affected to different degrees,

[1] E. G. Geisinger and K. Berlinghof, "Effect of Furnace Gases on Glass Enamels," *Jour. Amer. Ceram. Soc.*, **13** [2] 126–42 (1930).

[3] F. B. Ortman, "Composition of Kiln Gases and Their Effect on Terra Cotta Glazes and Colors," *Jour. Amer. Ceram. Soc.* **3** [6] 476–88 (1920).

the greens and yellows most and the reds and blues least. Little improvement was obtained by raising the temperature of the decorating kiln from 1350° to 1400°F. or by putting the ware through the kiln several times.

Although the decorating kiln was a muffle type, it had been in service for a number of years, and it was known (and verified by gas analysis later) that the muffle was by no means gastight. To shut down the kiln for repairs, however, meant a delay in production which could not be tolerated at the time. The kiln was provided with a recirculating arrangement at the entrance end which brought the combustion gases in direct contact with the entering ware at that point.

Although the decoration defect appeared and disappeared apparently in an unaccountable manner, it may be said in retrospect that its appearance was always associated with an increase in the contamination of the muffle gases with combustion products in the zone of high fire in the kiln.

The kiln was provided with a multiplicity of dampers and with recirculating fans and ducts, but these had been designed chiefly to permit the control of the temperature in the kiln and it was impossible to build up sufficient pressure in the muffle to prevent the entrance of combustion products. The pressure at the top of the combustion chambers was particularly high as a result of the expansion of the burning gases and the tendency of hot gases to rise. Actual tests also showed that opening vents in the top of the combustion chambers was the most effective if rather expensive way to reduce muffle contamination.

Analyses made of the muffle and combustion chamber atmospheres at various times showed that at some points the muffle atmosphere contained about 50% of combustion products.

(2) Possible Explanations

Although there is little information in the literature on the effect of kiln gases on decalcomania decoration, Andrews and Hertzell[4] indicate in their work on enamels that small concentrations of sulfur dioxide can exert a deleterious effect on some ceramic colors, and the present writers thought from the first that contamination of the muffle gases with sulfur dioxide was the most likely cause of the defect. Other suggestions, however, were advanced, which had to be considered. These suggestions included (1) the deposition of fine kiln dust on the fused colors, (2) a change in the temperature gradient caused by the higher ignition velocity of manufactured gas, (3) the introduction of a new type of size, and (4) volatilization of fluxes from the decoration.

(3) Laboratory Investigations

Laboratory experiments were made in the tube furnace mentioned previously as well as in a laboratory, gas-fired pot furnace in which whole saucers could be fired. The tube furnace was provided with a cartridge of manganese dioxide which could be inserted when an atmosphere free from sulfur dioxide was required.

Good decoration could be produced in an atmosphere free from sulfur dioxide, using either the old or new size if the decalcomania was oxidized rapidly or very slowly and then heated in a matter of a few minutes to 1400°F. and held there for one hour.

The oxidation of the decalcomania at an intermediate rate over a period of about 20 minutes to one hour resulted in a minutely broken decoration, which could be mistaken for the defect under examination and was a source of difficulty in some of the early experiments.

After considerable study, it was shown that the decoration was not appreciably affected by relatively large concentrations (40 p.p.m.) of sulfur dioxide below 1200°F. but was readily affected in the range of 1200° to 1600°F. A reverse reaction sets in above 1600°F., and initially defective ware could be fired to a good gloss in the presence of the sulfur dioxide.

The magnitude of the defect seemed to depend on the total amount of sulfur dioxide with which the decoration came in contact in the temperature range of 1200° to 1600°F., and it was estimated that 3 p.p.m. of sulfur dioxide in the muffle atmosphere was the maximum that could be tolerated in the time normally spent above 1200°F., which was two hours. This concentration was above that which would be produced by burning natural gas.

It was concluded that the defect was due to sulfur dioxide and that steps should be taken to reduce its content in the muffle atmosphere below 3 p.p.m. This reduction was possible by damper adjustment, fan repairs, and partial venting of the combustion chambers.

(4) Other Observations

In connection with the problem of reducing the concentration of sulfur dioxide in the muffle atmosphere, some experiments were made on the absorption of sulfur dioxide by lime compounds. It was found that lime would remove appreciable quantities of sulfur oxides from combustion gases containing as little as 7 p.p.m. of sulfur dioxide at 1420°F. Inasmuch as less than one-half pound of sulfur entered the decorating kiln per day, sending small lumps of lime through with the ware was a possible method of clearing the kiln. This method was not actually tried in practice although it was shown by analysis that the lime wash applied to the iron kiln furniture was converted almost wholly to calcium sulfate.

A microscopic examination of fragments of dinner plates fired in the laboratory showed that well-matured decoration was associated with a definite rounding of the sharp edges of the glaze, and it was suggested that this might be used commercially as a check on the operation of the decorating kiln.

It was found that the decoration could be fired under reducing conditions provided the decalcomania was first oxidized thoroughly at a low temperature. The colors, however, were different from those obtained under oxidizing conditions.

In one series of experiments, erratic results were

[4] A. I. Andrews and E. A. Hertzell, "Effect of Furnace Gases on Quality of Enamels for Sheet Steels," *Univ. of Ill. Eng. Expt. Station Bull.*, No. 214, 32 pp. (1930); see also *Jour. Amer. Ceram. Soc.*, **13** [8] 522–29 (1930).

obtained, which were traced to sulfur dioxide liberated by small pieces of insulating brick used as supports for the test pieces. If the ware was exposed for more than one hour at 1400°F. to 40 p.p.m. of sulfur dioxide, the glaze itself became dull and rough.

(5) Other Problems

Although the information obtained from the laboratory investigation was sufficient to explain the difficulties in the plant, there were still some matters requiring further investigation. For instance, the striking effect produced by such small quantities of sulfur dioxide requires further study. It is improbable that enough sulfate is formed to raise the fusion point of the color materially; in fact, under the microscope, the colors appear to have fused. The sulfates apparently alter the surface characteristics of the color and prevent it from "wetting" the glaze.

In one series of tube-furnace experiments, the mixture of laboratory gas and air was passed through a hot, fused silica tube instead of being burned in a flame. Good decoration was fired under these conditions although high concentrations of sulfur oxides were present. This raised the question as to whether sulfur trioxide and sulfur dioxide differed radically in their effect. When these experiments were repeated at a later date, only defective decoration could be produced. This problem was therefore postponed for further study.

IV. Summary

Blistered glostware, set in the open, and mat decalcomania decoration were encountered in the manufacture of semivitreous dinnerware following a change from natural gas to a manufactured gas which had a higher sulfur content.

It was shown that fifteen minutes of exposure at high fire to conditions slightly on the reducing side of the theoretical neutral point would produce the glost defect. Sulfur dioxide alone would not produce the defect except at relatively high concentrations, but its presence in the kiln may be a necessary condition to cause blistering.

Mat decoration was produced in two hours in the range of 1200° to 1600°F. if more than 3 p.p.m. of sulfur dioxide was present. The sulfur dioxide had little effect below this temperature range and above it the defect was corrected.

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Acknowledgment

Acknowledgment is made to Sovereign Potters, Limited, Hamilton, Canada, for their cooperation and financial support.

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CALCULATION OF MINERALOGICAL COMPOSITION OF FELDSPAR BY CHEMICAL ANALYSIS*

BY E. W. KOENIG

ABSTRACT

Formulas are given for the determination of the percentage amounts of microcline, albite, anorthite, kaolinite, muscovite, and free quartz in feldspars.

I. Introduction

Certain uses of feldspar in the ceramic industry demand values (indicating composition) which are not too readily apparent by observation from the chemical analysis. This is particularly true of the percentage of free quartz. A knowledge of the percentage of the other rock-forming minerals present is also essential in studies covering the chemical or mechanical separation of feldspar from free silica.

* Received January 31, 1942.

II. Present Procedures

Chemical procedures have been described for the direct gravimetric or petrographic determination of free quartz[1] which depend on the preferential solution of

[1] (*a*) F. H. Goldman, "Hydrofluosilicic Acid Method for Determination of Quartz," *Ind. Eng. Chem., Anal. Ed.*, **13** [11] 789–91 (1941); *Ceram. Abs.*, **21** [3] 70 (1942).
(*b*) W. R. Line and P. W. Arradine, "Determination of Quartz in Presence of Silicates," *Ind. Eng. Chem.*, **9** [2] 60–63 (1937); *Ceram. Abs.*, **16** [5] 160 (1937).
(*c*) Adolph Knopf, "Determination of Quartz in Dusts," *U. S. Public Health Reports*, **48**, 183–90 (1933).

SYMBOLS USED IN FORMULAS

A = % of H_2O as found		A' = mol. wt. of H_2O	(18.02)
B = " " SiO_2 " "		B' = " " " SiO_2	(60.06)
C = " " Al_2O_3 " "		C' = " " " Al_2O_3	(101.94)
D = " " CaO " "		D' = " " " CaO	(56.08)
E = " " Na_2O " "		E' = " " " Na_2O	(61.99)
F = " " K_2O " "		F' = " " " K_2O	(94.19)
U = " " albite	present	U' = " " " albite, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	(524.29)
V = " " microcline	"	V' = " " " microcline, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$	(556.49)
W = " " anorthite	"	W' = " " " anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$	(278.14)
X = " " muscovite	"	X' = " " "muscovite, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	(796.40)
Y = " " free quartz	"	Y' = " " " silica, SiO_2	(60.06)
Z = " " kaolinite	"	Z' = " " " kaolinite, $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$	(258.09)

the feldspar in fluoboric or hydrofluosilicic acid. All of these procedures are tedious and leave much to be desired from the standpoint of precision of results. These methods, moreover, do not include the determination of the rock-forming minerals other than that of free quartz.

Petrographic examination of thin sections or of powdered specimens of fused feldspar for the determination of free quartz has been used in the ceramic industry with excellent results,[2] but again the determination of the other probable constituents cannot be accomplished by this means.

Methods for the calculation of mineralogical composition from the chemical analysis are well known to every ceramist. Watkins[3] and Malinovszky, Panton, Staley, and Knight[4] have advanced formulas for these determinations. All of them are based on two-, three-, or five-component systems, and all make certain assumptions of questionable validity.

III. Composition of Commercial Feldspar

The mineral feldspar is essentially an admixture of microcline, albite, anorthite, kaolinite, and free quartz. Minor constituents, such as apatite, lepidolite, amblygonite, spodumene, epidote, calcite, magnesite, and fluorspar, are sometimes present and may be removed by selective mining and cobbing. The iron-bearing contaminants (sometimes found in minor quantities), such as pyrite, limonite, hematite, garnet, biotite, and tourmaline, are usually removed either during the mining operation or afterward by treating the crushed material by means of high intensity magnetic separation or froth flotation. Either of these latter purification treatments are also instrumental in the removal of the bulk of the muscovite mica, which might be present in the parent material in minor quantities, although conditions for the complete removal of this contaminant are critical. For this reason, a knowledge of the actual amount of this constituent present in the parent rock is helpful in the determination of the efficiency of the separation processes. The formulas which follow are therefore based on a six-component system.

IV. Proposed Method of Calculation

Inasmuch as definite molecular weights can be assigned to each of the rock-forming minerals and to the component parts of these minerals, it is possible to derive a series of formulas which will indicate the contribution of each of the component parts to the whole. From these data and from that offered by the chemical analysis of the sample, values for the individual rock-forming mineral may be obtained.

The percentage of Na_2O found by analysis obviously governs the percentage of albite in the sample under consideration; therefore

$$E = U\left(\frac{E'}{U'}\right).$$

Similarly, because the total amount of H_2O is contributed both by muscovite and kaolinite,

$$A = X\left(\frac{2A'}{X'}\right) + Z\left(\frac{2A'}{Z'}\right).$$

By transposition, the following series of equations may be evolved:

$$U = \frac{E'E}{U'}.$$

$$V = \frac{V'A}{2A'} - \frac{V'C'}{C'} + \frac{V'D}{D'} + \frac{V'E}{E'} + \frac{2V'F}{F'}.$$

$$W = \frac{D'D}{W'}.$$

$$X = \frac{X'C}{C'} - \frac{X'A}{2A'} - \frac{X'D}{D'} - \frac{X'E}{E'} - \frac{X'F}{F'}.$$

$$Y = B - \frac{2Y'A}{A'} + \frac{2Y'C}{C'} - \frac{4Y'D}{D'} - \frac{8Y'E}{E'} - \frac{8Y'F}{F'}.$$

$$Z = \frac{Z'A}{A'} - \frac{Z'C}{C'} + \frac{Z'D}{D'} + \frac{Z'E}{E'} + \frac{Z'F}{F'}.$$

The substitution of molecular weights and the simplification of these formulas give the following results:

$$U = 8.458E.$$

$$V = 15.442A - 5.459C + 9.923D + 8.977E + 11.815F.$$

[2] (*a*) G. H. McIntyre and M. Bozsin, "Rapid Determination of Quartz in Feldspar," *Ind. Eng. Chem., Anal. Ed.*, **12** [6] 326–28 (1940); *Ceram. Abs.*, **19** [8] 184 (1940).
(*b*) M. C. Booze and A. A. Klein, "Rapid Means for Determination of Quartz Content of Feldspars," *Jour. Amer. Ceram. Soc.*, **6** [6] 698–705 (1923).
(*c*) H. Insley, "Quantitative Microscopic Analysis of Commercial Feldspar," *ibid.*, **10** [9] 651–69 (1927).

[3] E. H. Watkins, "Why a Variation as Small as Three Per Cent of Silicon Oxide Content in Feldspar Will Cause Wide Variation in Workability of Porcelain Enamel," *Enamelist*, **2**, 16 (1925).

[4] A. Malinovszky, H. D. Panton, H. F. Staley, and F. P. Knight, Jr., discussion on "Free Quartz in Feldspar," *Ceramist*, **7** [2] 81–93 (1925); *Ceram. Abs.*, **5** [3] 81 (1926).

$$W = 4.960D.$$
$$X = 7.813C - 22.097A - 14.201D - 12.847E - 8.455F.$$
$$Y = B + 1.178C - 6.666A - 4.284D - 7.751E - 5.101F.$$
$$Z = 2.740F + 14.323A - 2.532C + 4.602D + 4.163E.$$

V. Discussion

The importance of accurate chemical analysis preliminary to the calculation of mineralogical composition cannot be stressed too highly. Seemingly minor deviations from the true values for any of the major constituents will be multiplied in the final analysis. This is also the case when rock-forming minerals are present other than those considered here. Despite these objections, the method appears to have merit in those cases where a complete mineralogical analysis is required or wherein the determination of any individual rock-forming mineral is of interest. The procedure is considerably more rapid than either the chemical or fusion methods for the determination of free quartz, and in the final analysis the results should have an equal or better order of accuracy.

Acknowledgment

The author is indebted to T. C. Carson, Jr., for aid in the current study.

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TESTING AND IMPROVING THE DRYING BEHAVIOR OF CLAYS*

By H. G. Schurecht and J. F. McMahon

Abstract

A simple test has been developed to measure the drying behavior of clays by noting the relative rate of flow of water through the clays as compared with the rate of evaporation from the surface. The addition of 0.2% of various chemicals to clays improved their drying properties. No one chemical was best for all of the clays, but the most effective chemicals varied in their reaction on different clays. Iron chloride exerted beneficial effect on most of the clays. A wetting agent, such as sodium chloride, hydrochloric acid, or soda ash, also improved the drying properties of certain clays.

I. Introduction

Although loss of ware due to cracking continues to be one of the major losses in the ceramic industry, the clays used are seldom tested for their drying behavior largely because there has been no simple standard drying test to evaluate this clay property. It is probably for this reason that many conflicting reports have appeared in the literature relating to methods of correcting the drying properties of clays.

The most common cause of drying cracks is the inability of water to travel to the surface as fast as it is evaporated. Phillips[1] has found that clays which tend to crack during drying also have a large moisture gradient between the center and surface of the ware. He also found that the addition of iron chloride and hydrochloric acid to these clays reduces this gradient and thereby improves their drying properties.

The mechanics of capillary movement of liquid water through a solid undergoing drying has been illustrated by Comings and Sherwood[2] and by Westman.[3] Water may also be removed by compression[4] as well as by evaporation, and it seems probable that the compression caused by capillary tension may squeeze some of the water from the clay.

II. Materials Used

The clays used in this study were as follows:

Clay No.	Name	Location
1	Hudson River blue clay	Goldrick's Upper Brick Yard near Kingston, N. Y.
2	Hudson River yellow clay	Goldrick's Upper Brick Yard near Kingston, N. Y.
3	Bottom bench black clay	Nassau Brick Co., Farmingdale, L. I.
4	Estavan shale	International Clay Products Co., Estavan, Sask., Canada
5	Redcliffe shale	Red Cliff Brick and Coal Co., Red Cliff, Alberta, Canada
6	Montreal clay	Montreal Terra Cotta Co., Ltd., Montreal, Que., Canada
7	Kentucky No. 4 ball clay	Mayfield, Ky.
8	Hancock clay	Hancock Brick and Tile Co., Findlay, Ohio
9	Delaware clay	Delaware Clay Co., Delaware, Ohio

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1942 (Structural Clay Products Division). Received March 25, 1942.

[1] J. G. Phillips, "Improving Properties of Clays and Shales," *Can. Dept. Mines, Bur. Mines, Dept. Mines & Resources, Pub.*, No. 793, 39 pp. (1938); pp. 3–18; *Ceram. Abs.*, **18** [6] 166 (1939).

[2] E. W. Comings and T. K. Sherwood, "Drying of Solids: VII, Moisture Movement by Capillarity in Drying Granular Materials," *Ind. Eng. Chem.*, **26** [10] 1096–98 (1934); *Ceram. Abs.*, **14** [10] 253 (1935).

[3] A. E. R. Westman, "Capillary Suction of Some Ceramic Materials," *Jour. Amer. Ceram. Soc.*, **12** [9] 585–95 (1929).

[4] H. G. Schurecht and C. M. Lampman, "Some Drying Properties of Clays: I, Effect of Small Imposed Loads on Rate of Drying of Some Clays," *ibid.*, **20** [8] 266–70 (1937).

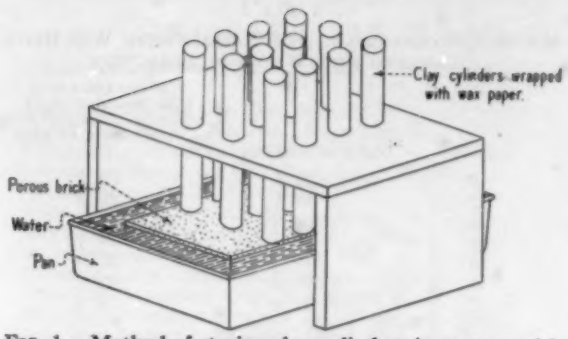

FIG. 1.—Method of storing clay cylinders in contact with water-saturated brick.

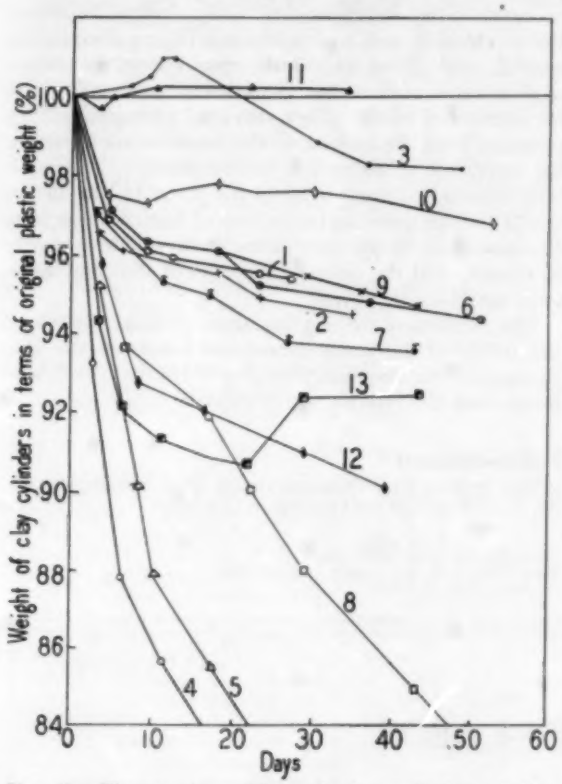

FIG. 2.—Changes in weights of clay cylinders during storage in contact with water-saturated brick.

Clay No.	Name	Location
10	Biglow clay	E. Biglow Co., New London, Ohio
11	Indiana clay	Indiana Drain Tile Co., Brooklyn, Ind.
12	Vannina clay	Vannina, Puerto Rico
13	Landrau clay	Landrau Road near San Juan, Puerto Rico

Clays Nos. 4, 5, 8, 12, and 13, which have extremely poor drying properties, usually crack badly even under carefully controlled conditions.

Clays Nos. 7, 2, 6, 1, and 9, when used without nonplastic admixtures, also crack in drying, although in some cases they may be dried safely under carefully controlled conditions.

Clays Nos. 11, 3, and 10 have comparatively good drying properties.

III. Experimental Methods

The clays were mixed with sufficient water to produce a normal plastic molding consistency. Clay cylinders, $^3/_4$ in. in diameter and 6 in. high, were extruded from each of the clays. These cylinders were immediately wrapped with wax paper to prevent water from evaporating from the sides. The ends of the cylinders, however, were left uncovered.

One end of the cylinder was set in contact with a water-saturated, porous insulating brick; the other end was exposed to the drying action of air at 20°C. (Fig. 1). Filter paper was placed between the specimens and the water-saturated brick to prevent the clay from disintegrating.

The clay cylinders were weighed after different periods of storage. The weights were expressed in terms of the original wet weight of the specimens.

The cylinders from seven of the clays were cut into sections about $^1/_2$ in. long after they had reached constant weight. The water content of each of these sections was then determined to study the moisture gradient from the end in contact with water to the exposed end.

IV. Results and Discussion of Results

(1) Change in Weight of Cylinders

Figure 2 shows that clays which lose the least weight when stored under the conditions of these experiments are also the safest drying clays and vice versa. Clays Nos. 11, 3, and 10, which changed in weight less than 3% after they were stored under these conditions for 40 days, were found to be safe drying in commercial use. When the weight of the clay cylinders showed slight change, there was evidence that the water passed from the wet end of the cylinder to the exposed end almost as fast as it was evaporated. The water, in such cases, was removed fairly uniformly from the center to the outside of the ware, and the water gradient from the wet surface to the exposed surface was therefore comparatively small. This type of clay shrinks uniformly throughout and does not crack after it dries.

Clays Nos. 1, 2, 6, 7, and 9 lost from 5 to 7% of their weight after they were stored under the experimental conditions for 40 days. It was apparent that the water did not flow from the wet end of the cylinder quite so fast as it was evaporated from the exposed end. If such clays were to be used for heavy clayware, they would have to be dried carefully, or some special treatment, such as that described in this paper, would have to be used to reduce the shrinkage gradients; otherwise the clays would be apt to crack in drying.

Clays Nos. 4, 5, 8, 12, and 13 lost more than 7% of water when they were stored under these conditions. All of these clays cracked badly in drying, and they were unsuitable in most cases for the production of ceramic products without special drying treatment. The passageways in these clays from the center to the sur-

face apparently are so small that they prevent the free movement of water from the center to the surface, and, as a result, the surface shrinks more rapidly than the center which causes cracking.

It is evident, therefore, that the change in weight of the cylinders, when the bottom is stored in contact with water-saturated porous brick, may be used to measure the drying behavior of clays. Those clays which show the least loss in weight in general are the safest drying clays, whereas those which lose considerable weight are usually poor drying clays; this relationship offers a satisfactory procedure for a rapid determination of the drying characteristics of clays.

(2) Water Content of Clay in Contact with Water-Saturated Brick

Although clays, which contain high water of plasticity, in general may possess poorer drying properties than those with low water of plasticity, there are many exceptions to this rule. Clay No. 5, for example, which has 34.29% water of plasticity, has a strong tendency to crack during drying. Clay No. 7, however, has a water of plasticity of 38.84%, but it has better drying properties than clay No. 5.

The water content of the section in contact with the wet brick apparently becomes much higher than the normal water of plasticity for certain poor drying clays. Clays Nos. 4, 6, and 5 are examples of this type (Table I). The portion of these clays stored in contact with the wet brick also swelled, indicating that they may contain small percentages of montmorillonite or other clay minerals which swell in contact with water.

Clays Nos. 1, 2, and 7 had less water in the section in contact with wet brick than the normal water of plasticity and most of them were good drying clays.

(3) Effect of Chemicals

The addition of chemicals changed the rate of drying under these storage conditions. Ferric chloride, hydrochloric acid, and wetting agents were most effective in most cases in improving their drying behavior. Ferric chloride and hydrochloric acid are flocculating agents, and these chemicals would produce larger agglomerates of fine clay particles as well as increase the number of voids. They also tend to open capillary passages from the interior to the exterior and to reduce the resistance of water flow to the surface. The capillary tension necessary to draw the water to the surface would thus be decreased; the rate of flow of water from the interior to the exterior of the ware would be greatly increased; and the drying properties of the clay, therefore, would be improved.

The addition of the wetting agent probably increased the ability of the water to wet and penetrate the finer passages in the clay and thus also facilitated the flow of water from the interior to the exterior of the ware.

TABLE I

WATER CONTENT OF CLAY IN CONTACT WITH WET BRICK COMPARED WITH WATER OF PLASTICITY

Clay No.	Water of plasticity (%)	Water content of bottom portion of cylinder in contact with water-saturated brick (%)
1	26.7	25.1
2	30.5	29.4
3	38.8	44.4
4	45.4	134.7
5	34.3	37.3
6	39.3	42.1
7	38.8	38.1

Acknowledgment

The writers wish to acknowledge their indebtedness to M. E. Holmes for suggestions in this work.

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ALFRED, NEW YORK

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